
**Calcium Magnesium Acetate (CMA)
Production: An Assessment of
Process Technology**



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Calcium Magnesium Acetate (CMA) Production: An Assessment of Process Technology

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Abstract:	Calcium magnesium acetate is a promising alternative to rock salt for deicing roads, but is prohibitively expensive. The report contains a technical and economic assessment of the possibility of producing a large quantity (1 million tonnes per year) of CMA in Ontario at a cost of less than \$350/tonne. Two basic approaches to the commercial production of CMA were identified: i) the production of acetic acid and its reaction with lime, and ii) the bacterial production of "acetate" from sugars in the presence of calcium and magnesium ions. The production of acetic acid by methanol carbonization combined with a drum pelletizer for reacting the acetic acid with lime to produce CMA was identified as the preferred process. When using natural gas as the basic raw material, and proven technology the estimated production cost was \$303/tonne. substituting municipal solid waste as the primary feedstock gave an estimated production cost of about \$340/tonne based on a tipping fee of \$30/tonne or \$305/tonne at a tipping fee of \$50/tonne (assuming the successful scale up of gasification technology). A comparative assessment of producing CMA directly from bacterial conversion of corn showed this approach not only to be more expensive, but considerable technical difficulties exist in scaling up laboratory size fermentors to commercial production.
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Sheridan Technical Associates Inc.

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Summary and Conclusions

Calcium Magnesium Acetate (CMA) shows promise as a road deicing agent to replace salt (sodium chloride) providing a large tonnage can be produced cheaply (10^6 tonnes/year at <\$350/tonne).

A full review of the literature has failed to reveal a "commercial" process for this scale of production. There has been minor production in the U.S. to provide material for road deicing. Chevron currently produces CMA from purchased acetic acid and dolomitic lime and sells the product at approximately \$1100/tonne.

Two basic approaches to the commercial production of CMA have been identified:

- the production of acetic acid and its reaction with lime
- the bacterial production of "acetate" from sugars in the presence of calcium and magnesium ions

The Ontario market size dictates the need for dedicated production facilities for either approach.

After reviewing the various commercial processes for acetic acid manufacture; butane oxidation, acetaldehyde oxidation and methanol carbonylation, the last was chosen for more detailed study. In addition, a drum pelletizer process was selected for reacting acetic acid and lime to produce CMA pellets (There is limited commercial data on this processing step).

The pelletizer was combined with the methanol carbonylation route into a conceptual process design to produce 10^6 t/year of CMA in Ontario using natural gas as the basic raw material. The estimated production cost of \$303/t provides a benchmark for assessing other processing schemes.

The possibility of substituting Ontario based raw materials for natural gas in this processing scheme was investigated. A similar sized process arrangement using Municipal Solid Waste (MSW) as the primary feedstock gave an estimated production cost of about \$340/t based on a tipping fee of \$30/t. An increase in the tipping fee to \$50/t reduced CMA production costs to \$305/t. Wood appears to be a somewhat less attractive feedstock source.

A comparative assessment of producing CMA directly from the bacterial conversion of corn showed this approach to be more expensive. (These data were based primarily on laboratory scale experimental work carried out in the U.S.) A much cheaper sugar source in sufficient quantity and major process improvements will be required to make this an economically competitive route at the present time.

Data on newer chemical routes have also been reviewed and although some show promise for providing a more economic process, a significant development effort would be required.

It is concluded that using current technology, the natural gas to acetic acid to CMA route, is the most economic, however the partial utilization of MSW and other inexpensive sources of combustible biomass may offer an environmentally attractive alternative. These results are summarized in the attached Table.

Options for the Manufacture of one million tonnes/year
Calcium Magnesium Acetate in Ontario

<u>Route</u>	<u>Chemical</u>		<u>Fermentation</u>
Principle Feedstock	Natural Gas	MSW/Biomass	Corn
Capital cost estimate \$MM	538	755/694	521
Proven Processes & capital cost	94	46/51	25
Process requiring scale-up	CMA 2 - 126 t/hr	CMA 2 - 126 t/hr	Fermentation Pilot Scale - 126 t/hr
Outstanding issues	Acetic Acid Licence. CMA Integration	Acetic Acid Licence, CMA Integration MSW Availability & Composition. Gasification technology availability	Feasibility of pilot scale fermentation. High Energy demand.
% Carbon utilization as CMA	71.8	54.3	28.7
Production \$/tonne	303	341/428	530
Spin-off	none	Reduces volume of MSW	Utilizes excess corn

Technology Review

1/ Introduction

CMA has been identified as the most promising, non-corrosive, environmentally benign alternative to rock salt as a deicing chemical. Unfortunately CMA presently costs at least 25 times as much as salt on the basis of small scale pilot production.

The objective of this technology review is to evaluate present and possible chemical and biotechnical processes to determine if opportunity exists for Ontario industry to produce CMA to the existing specifications for use as a deicer at a cost less than \$350/tonne (1988 prices). As a guideline, production costs will be based on a plant producing 10^6 tonnes/a which approximates to the potential Ontario requirements.

Dolomitic limestone, one of the basic ingredients is plentiful and cheap in Ontario; the other, acetic acid is not. Acetic acid is currently traded as a commodity chemical and is normally supplied under a long term contract. The acetic acid requirement (800 kt/a) for CMA manufacture, however, will be too large for the current production capacity. Indeed the projected Ontario market for CMA will be equivalent to approximately 15% of the world capacity for acetic acid (1). This is equivalent to about 50% of current U.S. capacity (64% of actual production, or 84% of European production). Canada has one producer of acetic acid, Celanese at Fort Saskatchewan in Alberta, their capacity (est. 365 kt/a) would obviously be insufficient for CMA production.

Hence, large scale production of CMA will require the construction of major new plants, and any procedure based on purchased acetic acid will be impractical because the size of the demand, if it could be met, would boost the price above the economic level.

This report examines the options available for the economic production of CMA and assumes that new capital construction will be required to achieve this. It is assumed that the Ontario market will be approx. 1×10^6 tonnes/year in terms of sales to the Ontario Ministry of Transportation and municipalities in the province. The possibility of export sales is not considered. New York, Michigan, Ohio, Pennsylvania and Quebec each use similar quantities of salt to Ontario.

This technology review is divided into subsections dealing with:

- Proven commercial processes for acetic acid manufacture
- Conversion of acetic acid to CMA
- Possible routes from renewable resources
- Newer chemical routes to acetic acid/CMA

2/ Manufacture of Acetic Acid

Acetic acid has been and still is manufactured commercially by several alternative processes and alternatives are still being sought. Each of the processes currently in use will be reviewed.

2.1/ Carbonylation of Methanol

This process was developed by Monsanto and is based on earlier work by British Celanese (2), I.G. Farben and others (3). It is the current preferred process for acetic acid manufacture and all new acetic acid plants are using this technology.

The basic chemistry is simple involving the introduction of carbon monoxide into the methanol molecule.



The preferred approach to methanol carbonylation is based on catalysis by rhodium complexes (4). These catalyst systems allow effective reaction at much lower temperatures and pressures, e.g. 150 - 200°C under 3300 - 6600 kPa (33 - 65 atm.) than the earlier technology based on a nickel iodide or copper and cobalt in the presence of iodine (5).

At 100% conversion, methanol selectivity to acetic acid is claimed to be 99% and only a very small concentration of the noble metal is needed, e.g. from 10^{-4} to 10^{-2} mol/litre.

The reaction kinetics are reported to be first order in methyl iodide and the rhodium complex with reaction rate (r) given by:

$$r = k [\text{CH}_3\text{I}] [\text{Rh complex}] \quad \text{where } \Delta E = 61.4 \text{ kJ/mole}$$

the rate constant (k) is $3.5 \times 10^6 e^{-\frac{\Delta E}{RT}}$ litres/mol/s. This shows the reaction to be quite fast, therefore the reactor sizes need not be excessive even for relatively high capacity plants.

The feed methanol is usually diluted with water to suppress methyl acetate formation and to increase conversion. The water however, interacts with carbon monoxide to furnish hydrogen and carbon dioxide, a factor limiting its addition to around 30%. The reaction product is cooled to 15°C and the pressure is lowered to 200 kPa (2 atm.) to remove the waste gases, chiefly methane and carbon dioxide.

Low boiling by-products are removed by distilling up to 80°C. These are mainly dimethyl ether, methyl acetate, acetaldehyde, butyraldehyde, and ethyl acetate and are normally recycled to the carbonylation reactor and thus do not present by-product disposal problems. The crude acetic acid is flashed overhead and the catalyst recovered from the base of the fractionator and recycled to the reactor. The crude acid is dehydrated and further fractionally distilled to remove heavy ends and give glacial acetic acid. Chief impurities are organic iodides, derived from catalyst residues, and propionic acid. Most of the latter is retained in the residue from the final distillation. A typical plant flow sheet is shown in Figure 1 (6).

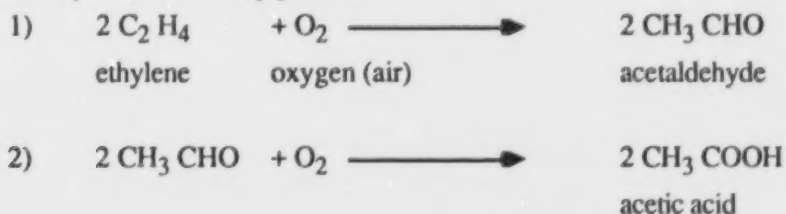
2.2/ Acetaldehyde Oxidation

This process is still extensively used in Europe. Capacity in North America has been shut down in favour of the methanol carbonylation route.

The process involves the direct air or oxygen oxidation of liquid acetaldehyde in the presence of manganese acetate, cobalt acetate, or copper acetate. The feed acetaldehyde in turn being usually derived from the air oxidation of ethylene in the presence of palladium and copper chlorides.

Ethylene is a major petrochemical produced from the pyrolysis of ethane or hydrocarbon liquids. Limited amounts of ethylene may also be available in refineries.

The chemistry of this two step process is:-



The yield of acetic acid on acetaldehyde is reported to be 95%.

In normal practice, air is sparged into a 5 to 15% solution of acetaldehyde in acetic acid in the presence of dissolved manganese acetate as catalyst. Conditions are usually 50 - 80°C under 800 - 1000 kPa (8 - 10 atm.) pressure. Cobalt acetate or solid phosphomolybdic acid may also be used as the catalyst. Copper ions will also act as catalyst but tend to cause the formation of acetic anhydride, which increases the corrosion rate in the reaction and purification systems.

The gaseous products from the reactor are scrubbed with water and recycle acetic acid before venting the waste nitrogen and by-product carbon oxides. Unreacted acetaldehyde is recovered and recycled. The crude acid is fractionated to remove methyl acetate. This could be sold primarily for use in paint removers; however, it may be contaminated with acetone, another by-product. The residual acetic acid is dried using azeotropic distillation with ethyl acetate and further fractionated to free it from the catalyst and give glacial acetic acid. The bottoms fraction containing the catalyst is recycled to the acetaldehyde oxidation reactor usually after treatment with water and an organic solvent to remove the ethylene glycol diacetate and tars, etc.

The chief impurities are formaldehyde and formic acid. If the acetaldehyde feed was obtained from ethylene, the crude acid may contain ethylene glycol diacetate obtained from traces of ethylene oxide in the feed. This can be further transformed into vinyl acetate in the final work-up.

When very pure acetic acid is required, a final purification involving distillation in the presence of potassium permanganate, sodium dichromate, or similar oxidants is carried out. Permanganate is more expensive than dichromate but oxidizes a wider range of impurities. The amount of aqueous potassium permanganate is adjusted to reduce the acetic acid concentration from 100.0 to 99.75%. This diminishes the corrosiveness of the product while removing traces of contaminants. This final treatment is also applied to acetic acid produced by other methods.

The mixtures involved in this process are highly corrosive and the plant costs reflect the extensive use of stainless steel.

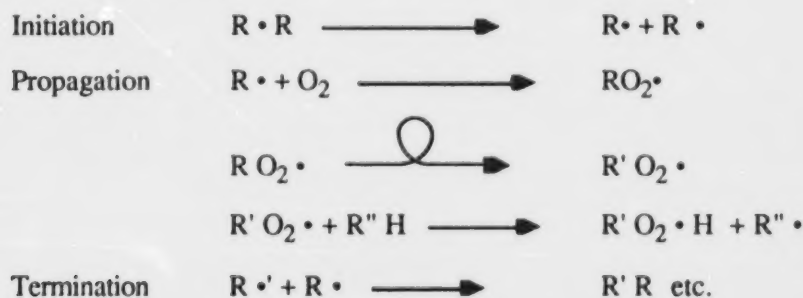
Unit start-ups require considerable care to prevent the build up of explosive peracetic acid. It is unlikely that any new acetic acid capacity will be built using this method. Acetic acid is no longer made by this route in North America, the last unit was shut down in 1984. A typical flow sheet is shown in Figure 2 (6).

2.3 / Butane/Naphtha Oxidation

Butane oxidation is still a major route to acetic acid in North America, although on a worldwide basis it probably accounts for less than 5% of installed capacity. Outside North America naphtha oxidation is more common.

The first liquid-phase catalytic oxidation of n-butane plant was brought on-stream by Celanese in 1952 at Pampa, Texas. Other similar plants operated by The Distillers Co., Ltd., Chemische Werke Huels, and in the Soviet Union followed in quick succession. Naphtha is more readily available in most parts of the world than is butane, and its oxidation can be effected at a lower temperature and pressure. The product composition from naphtha, however, is far more complex and the separation of acetic acid is more costly. Both processes are inherently similar.

The reactions involved are typical of hydrocarbon oxidation chemistry. The metal catalyst functions to generate an alkyl radical from the hydrocarbon. This species reacts with oxygen, undergoes intramolecular rearrangement to produce ultimately acetic acid and another free radical which again reacts with oxygen (the propagation steps). Eventually two radicals combine to form stable by-products (termination).



In a typical operation, butane is dissolved in acetic acid along with a suitable homogeneous catalyst, e.g. cobalt, chromium, and vanadium or manganese acetates, and sparged with air at 100°C and from 1000 - 5000 kPa (10 - 54 atm.) pressure (7). The salts of stainless steel constituents are quite effective catalysts and some processes operate without added homogeneous catalyst.

The oxidate is a complex component mixture including water generated by the reaction. Product separation is a major operating cost for the process and markets have to be available for the by-products.

The major low boiling constituents are ethyl acetate, methyl ethyl ketone and methyl vinyl ketone, along with traces of aldehydes and other esters. In the dehydration column, some acetic acid and formic acid are entrained with the water. Formic acid-water mixtures form a maximum boiling azeotrope, which seriously complicates the separation.

Substances boiling higher than water in the mixture are chiefly the lower carboxylic acids, e.g. formic acid, acetic acid and propionic acid. Formic acid and acetic acid may be distilled easily after the water has been removed. Propionic acid and butyric acid are usually contaminated with acrylic acid, which has a boiling point within a degree of that of propionic acid. A number of carbonyl compounds are present in low concentrations, including biacetyl, acetylacetone, acetonylacetone, butyrolactone, and a collection of still higher boiling substances. Needles of succinic acid sometimes crystallize from the high-boiling mixture. A typical plant flowsheet is shown in Figure 3. Many variations of this layout are possible depending on the degree of recycle and the opportunity to market the by-products.

Hydrocarbons higher than butane, e.g., pentane, hexane, or heptane, often yield oxygen-containing heterocyclic compounds, e.g. tetrahydrofurans. They also produce substantially greater quantities of dibasic acids than butane under similar operating conditions. Adipic acid, glutaric acid, and succinic acid are often present.

Butane gives higher yields of acetic acid than the higher paraffins. By-product credits for recovered formic acid, propionic acid, and butyric acid may alter the cost of making acetic acid by this route, however, the higher molecular weight products may be recycled and only acetic acid accounted as the product.

Because of the multiplicity of products it seems unlikely that it is an economic way of making CMA unless either a good market can be found for the by-products or a satisfactory deicer can be made from essentially the mixture of the acids as produced.

2.4/ Bacterial Fermentation

Acetic acid in the form of vinegar has been produced since ancient times by a bacterial fermentation process. All vinegar sold in Canada must be produced by fermentation of ethanol. However the high cost of the ethanol feedstock whether produced naturally by yeast fermentation of sugars or synthetically from ethylene have made it impractical to produce glacial acetic acid by this route.

Operations are further hampered by the massive quantities of water to be handled. Vinegar is approximately 6% acetic acid although higher concentrations could probably be made.

Nevertheless much research and development has gone toward the utilization of agricultural products to generate ethanol, for use as an alternative fuel supplement and octane booster.

Most of this activity has been generated by the "gasohol" program in the U.S. Both farm crops (surplus corn and wheat, etc.) and wastes from canning and other food processing operations have been studied. Several large scale plants are in operation and ethanol is available at about \$460 Cdn./tonne in the U.S. There is a federal incentive (subsidy) which provides some ethanol at about \$210 Cdn./tonne.

If ethanol were generally available at this latter price, then bacterial fermentation to acetic acid by *Acetobacter aceti*, referred to above, could be an economic route:



Certain moulds are also capable of this reaction, e.g. *Mycoderma aceti*, formally used in making vinegar. This oxidation can also be carried out chemically.

It is possible that the use of genetic engineering may improve the performance of acetobacter. Indeed a recent paper claims up to 9.6% acetic acid concentration at twice the normal production rate by cloning a membrane bound aldehyde dehydrogenase gene in an acetobacter (60). Furthermore, a survey of acetobacter used in submerged vinegar fermentation revealed they carry between 3 and 11 plasmids per cells. The number and function of plasmids can be adjusted by genetic engineering techniques. If any of these plasmids control acetic acid production further improvements to the fermentation should be possible.

A recent study (9) has reported the direct production of acetic acid at pH 4.5 from sugars using the thermophilic bacteria *Clostridium thermoaceticum*. Solvent extraction directly from the fermentation, for example, ethyl acetate could be developed; this may increase fermentation rate and reduce the energy required to concentrate the acid. Membrane separation may also be possible but experience suggests high capital cost and fouling would make their use impractical.

Many forest waste materials, e.g. pulpmill liquors, sawmill chips and dust, newsprint, etc., have also been examined as sources of carbohydrates for fermentation. None has proven competitive solely as a means for acetic acid or ethanol production, although technically acceptable routes have been worked out. Whilst the cost of the raw material is relatively low, the combined difficulties of

concentration, purification, and the high capital investment for a low-capacity plant, have made these routes noncompetitive (1).

2.5/ Older Methods

Until relatively recently wood distillation was the principal source of acetic acid. It is still employed in the Soviet Union as a means for producing industrial quantities of acetic acid, but the process depends heavily on various by-product credits to justify the high investment and operating expenses. Acetic acid by these routes can be made more attractive by allocating greater costs to the production of paper or lumber, or by applying more realistic costs to environmental improvements resulting from waste utilization.

The destructive distillation of woods, generally hardwoods, at temperature up to 500°C results in the thermal breakdown of the basic wood structure to give four basic components; charcoal, pyroligneous acid liquor, tar and a mixture of non-condensable gases. The pyroligneous acid is further fractionated and refined to yield the acetic acid as well as water, tar, wood oils, etc. In one process the acid is purified by treatment with lime to give calcium acetate before recovering neutral compounds (methanol, acetone). Glacial acetic acid is then produced by heating calcium acetate with sulphuric acid. The impure calcium acetate could be isolated but it is not possible to produce the quantity required by this process. The disposal of all the by-products would also pose a problem.

2.6/ By-Product Acetic Acid

Acetic acid is a by-product in several currently commercial processes. It is usually found in dilute solution. None of these by-product sources would produce acetic acid in sufficient quantity.

Acetic acid is found as a by-product in;

- a) Converting polyvinyl acetate to polyvinyl alcohol.
- b) The allyl alcohol-peracetic acid route to glycerin.
- c) In peracetic acid production.
- d) In aspirin manufacture.
- e) From various acetylation reactions.

It is also produced as a coproduct in one process to produce terephthalic acid.

3/ Production of CMA from Glacial Acetic Acid

The above review has dealt with the production of acetic acid, and obviously further additional processing involving both the acid and a calcium and magnesium source will be required to produce CMA.

Dolomitic limestone is the only feasible source of magnesium and calcium in the quantities required. The reaction of acetic acid with dolostone or dolomitic lime to produce CMA is a significant processing step. Two studies have been done for the Federal Highway Administration in the United States (10, 11). Both these studies have reacted unslaked lime (Dolime) with glacial acetic acid.

The first scheme uses two slaker/dissolvers to ensure complete solution of both the calcium and magnesium (which dissolve at different rates). The effluent is essentially at 28% solution of CMA (saturated at 100°C) which is freed of water in a rotary drum dryer and the solid CMA is flaked, crushed and screened to size.

The second study (Gancy) uses a drum pelletizer to directly react and dry the unslaked lime and approx. 80% acetic acid. The product has a narrow size distribution which can be adjusted by varying the operating parameters of the drum pelletizer. Operating costs are claimed to be lower than in the case above principally because far less water requires to be vapourized.

Chevron manufacture CMA (estimate 3000 t/a) as the chemical "Ice-B-Gon" at a converted fertilizer plant in Kinawix, Washington using purchased glacial acetic acid, dolime and magnesium oxide. Presently there are no published data on this plant.

The University of Alaska (12) has studied the dissolution of limestone in diluted acetic acid to produce an essentially saturated solution of Calcium Acetate (CA) (28%). They recommend the use of acetic acid produced by current technology but before it is concentrated to give glacial acetic acid. Their process essentially dissolves limestone in a slight excess of acetic acid at 70°C with a mean residence time of 3 hours. Reaction is 75% complete under these conditions. The excess limestone and solid non-reactables are filtered off whilst excess acid can be recovered from the CA solution. The Alaska report does not address the production of solid CA from this solution.

Two other attempts to prepare CMA for use as a road deicer are reported. The Iowa Department of Transportation (13) used a modified concrete mixer to react glacial acetic acid, hydrated lime in the presence of dry concrete sand and an agent to promote the adhesion of CMA to sand particles. Excess acid was always used which gave an ultimate product containing free acid. This was both corrosive and had an acetic acid odour. The excess acid was removed at 105°C but the adhesion of the CMA to the sand was lost and a dusty product resulted.

The Maine Department of Transportation (14) study involved reacting dolomitic limestone with dilute acetic acid (10%). At ambient temperature, reaction was slow and incomplete leaving an acidic product and required further neutralization with high magnesium quicklime to pH 9. Solar drying was unsuccessful.

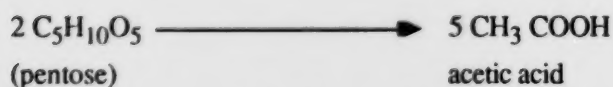
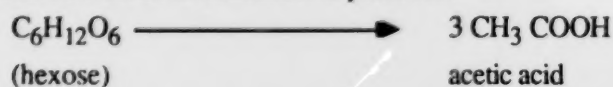
4/ Possible Routes to CMA from Renewable Resources

During the energy crisis in the 1970's, the U.S. Government placed restrictions on the use of petroleum derived materials (i.e. derived from natural gas and crude oil). In addition, major efforts were made to develop other sources for fuel and chemicals. "Biomass" and coal were considered the most feasible alternatives and large research programs were initiated to develop alternative processes. The "gasohol" program focussed principally on the fermentation of corn derived starch/sugars, and the Great Plains Coal Project was directed to using Wyodak type coals.

The decision to investigate the large scale production of CMA therefore focussed on the use of biomass and specifically on "homoacetate bacteria", bacteria that convert sugars to acetate ion. This type has been used to produce acetic acid, but generally they function best in controlled pH situations. The control of pH by the addition of lime leads to the by-product, calcium acetate.

Anaerobic degradation of organic compounds occurs widely in nature, such as in soils, muds, sediments, sewage sludge digestors, composts as well as the digestive tract of all animals. Normal ends products of this action are methane and carbon dioxide, however "acetate" is an intermediate in virtually all cases. In most natural habitats the observed end products are the result of the interactions of a wide variety of bacteria and include both "acetate" forming and "acetate" consuming bacteria.

Certain bacteria have the ability to convert sugars almost exclusively to "acetate" and furthermore many will convert both hexoses and pentoses.



Note all of the carbon present in the sugar is recovered in the acetic acid.

Such bacteria are called acetogenic and although the subject of research for many years, only relatively recently have they received more general interest and pure cultures of several species have been isolated. *Clostridium thermoaceticum* was the earliest and others isolated have been *Acetogenium kivui* and *Clostridium thermoautotrophicum*, all of which have been evaluated by the University of Georgia (15) for CMA production ability. These bacteria are all thermophilic and

function best above 50°C. (Most bacteria are mesophilic and operate at 30-40°C). According to the University of Georgia report (15), 14 different homoacetogenic bacteria have been isolated and described.

4.1/ SRI Study

The first attempt to utilize *C. thermoaceticum* to produce calcium magnesium acetate was by SRI (16). Their experimental work was not very successful giving low glucose to acetate yields and apparent contamination of their culture with foreign thermophilic bacteria.

Nonetheless a basic process scheme was worked out based on corn grain as the sugar source and assuming 91% conversion to glucose and subsequent fermentation at 75% theoretical acetate yield. A scheme was also costed using high glucose corn syrup as the basic sugar source.

In the basic scheme corn grain is dispersed in water to form a mash containing 25% solids which is adjusted to pH 6 by the addition of a minor amount of lime. The α -amylase enzyme is added and the mash cooked at high temperature before cooling to around 90° and holding at this temperature for approximately 1 hour. The α -amylase effects the conversion of starch to maltose. After further cooling to 60°C the pH is adjusted to 4.5 with sulphuric acid then glucoamylase (a maltase enzyme) added to affect the conversion of maltose to glucose. This latter step commonly takes 48 hours.

This glucose slurry is further diluted with water to give approximately 8% glucose solution and fermented at 60°C in continuous fermentors with *C. thermoaceticum*. Average residence time is 13.3 hours (LHSV = 0.075). The pH is kept at 6.0 by the continual addition of "dolime" slurry. Care is taken to maintain anaerobic conditions. Carbon dioxide is a by-product which is not recovered. Additional lime is added to the fermentor effluent to raise the pH to 9 and the insolubles (corn solids and bacterial cells) allowed to settle. After filtering the cake is dried to produce an animal feed by-product. Its suitability for this purpose remains to be verified.

The dilute CMA solution, assumed to be 7% in CMA, is concentrated in evaporators before drying and crushing. The block flow diagram of the process given by SRI is shown in Figure 4.

4.2/ University of Georgia Study

This report significantly extends the SRI study to include the three bacterial types mentioned above. Two strains of each type were evaluated and mutant (improved) strains developed. The characteristics of four different fermentor designs, and operational modes were also studied; continuous, continuous with cell recycling, continuous rotary and batch.

In addition the effects of various operating conditions on the performance of these bacteria were determined. In general these organisms were found to be quite tolerant of wide variations in feed concentrations, for example, glucose feed concentration up to 20%. However at high glucose concentrations the reaction rate was low and the ultimate utilization of the glucose far from 100%. Optimum rates were obtained at 1-2% glucose. This gave low concentration of CMA which required an excessive amount of water to be removed to obtain solid CMA. Only in the case of a pure batch fermentation did a CMA in broth concentration reach the 7% assumed in the SRI report. A CMA process design by the University of Georgia actually assumed an 11.24% CMA concentration but this was achieved only after an extremely long fermentation period. The savings in energy because of reduced water evaporation were more than offset by the increased cost of the fermentors and the energy required to maintain them at 60°C.

In all fermentation reactions it is necessary to maintain a medium with trace minerals etc., for the viability of the culture. The medium used for the investigative part of the University of Georgia's program is illustrated in Table 1. Note the glucose concentration is 10 g/l (1% w/v). In the production of CMA, some of these trace minerals end up as impurities in the CMA.

The University of Georgia produced 150 lbs. of CMA by doing eight 400 l fermentation runs using the reaction medium shown in Table 2. Hydrolyzed corn starch was used in place of pure glucose used for laboratory experiments, as assumed in the SRI assessment (16). Three separate bacteria were used, *C. thermoaceticum* wild strain, *C. thermoautotrophicum* 701/5 P-N A-20, and *C. thermoaceticum* Wood EMS-90. The last two were mutant strains produced with pyruvate and nitrous acid, and methane sulphonic acid respectively. The *C. thermoautotrophicum* gave the best yield of CMA. These experiments are the first successful, large scale attempt at producing CMA by this bacterial fermentation method. The results are shown in Table 3. The best acetate/glucose ratio was approximately 2.5 with the average of the eight runs being 1.89, well below the theoretical value of 3. Productivity was 9 g/l/d and the final CMA concentration 39.5 g/l or around 4% w/v.

4.3/ New York Study

A recent report prepared for the New York State Energy Research and Development Authority (17) has investigated "halophilic" bacteria to produce increased levels of CMA in the fermentation broth based on low grade organic feedstocks. Most of the work was performed using acid cheese whey as the sugar source and a mixed culture of halophilic bacteria obtained from sediments of the Great Salt Lake in Utah acclimatized to lower sodium chloride concentrations. These bacteria were mesophilic giving optimum growth around 37°C. Previous work above used thermophilic bacteria at 55-60°C. The results are set out in the summary to the report.

"Semi-continuous anaerobic digestion experiments utilized pH control, substrate concentration, and operation at 10- and 20-day hydraulic retention times to determine conversion efficiencies and acid production. The results of halophilic anaerobic fermentations using acid whey substrate produced mixed total volatile acid concentrations of 3.0 percent, by weight, resulting in a 3.75 percent CMA in solution. Greater than 75 percent conversion of acid whey substrate to acids was achieved during semi-continuous operation. A mixed pool of acids were produced with acetic, propionic, and butyric acids occurring in nearly equal concentrations.

Acid concentrations of 3.5 percent, by weight, were achieved using milled whole kernel corn as a feedstock, resulting in 4.4 percent CMA in solution. Greater than 50 percent conversion of corn to acids occurred of which acetic acid was the predominant species of acid formed. Based upon the results of the semi-continuous operation, a minimum hydraulic 20-day retention time (HRT) would sustain high conversion rates. Longer HRTs would most likely improve acid production and result in higher conversion efficiencies".

This production of mixed acids is a step away from the earlier studies and the calcium and magnesium salts derived from such a mixture would require further testing for their deicing efficiency and their environmental acceptability. Calcium butyrate, for example, has only limited solubility in water and the butyric acid liberated by the action of acid (acid rain) on the salt has a very unpleasant odour.

4.4/ Other Studies

Several bacteria that produce "acetate" have been described above, many other bacteria also produce acids. In sewage sludge, 22 non-methanogenic microorganisms are known to produce acid. This mixed culture can tolerate an acid concentration of 4% and produce up to 0.8 g acid/gram glucose with a productivity of 1.7 g/l/h (18). These figures are quite good, however the product is not pure acetic acid but a mixture of acetic, propionic and butyric acids, which may be unsuitable for making deicer. Most papers dealing with mixed cultures report the same good acid production rate but a mixed product.

Some bacteria have the ability to ferment either sugars or utilize syngas to produce acid. A recent paper (19) studied 6 different bacteria with syngas but in general found the rate of acid production to be between 1/20 and 1/100 of the rate using fructose as carbon source. Conditions were generally 70 psig gas pressure at optimum temperature for the culture. As above the product was mainly acetic acid but significant amounts of butyric acid were also produced.

A second paper (20) describes the use of *Peptostreptococcus productus* for this synthesis.

The isolation of *Clostridium fervidus* from a hot spring in New Zealand has been reported (21). This thermophile will ferment a range of carbohydrates including apparently xylan and starch to give acetate as the major fermentation end product. By-products include carbon dioxide, hydrogen and minor amounts of other acids and ethanol.

A second paper in the same volume reports on another organism capable of acetate production *Sparomusa paucivorans* (22). This new anaerobic species is capable of producing acetate from methanol and will grow on other C1 compounds, pyruvate, glycerol, lactate, serine and mono and dialcohols.

Ethanol and acetic acid in equimolar amounts have been reported as the only two carbon products of *Cellulomonas sp.* when using cellulose as the substrate (23). These products were identified when this organism was submitted first to aerobic growth and then anaerobic growth.

In none of the abstracts of these last three references are details given and it is doubtful that the potential of any of these bacteria for use in an industrial process has been assessed. A closer evaluation of the available data on these and perhaps other bacteria may justify further research

particularly if they can utilize raw carbohydrate sources without the need for preprocessing e.g. wood.

4.5/ Acetate from Wood - Minimum By-Product Yield

Wood is composed chiefly of cellulose, hemicellulose and lignin, the cellulose component is primarily a "polyglucose", which, could it be readily depolymerized, would provide an abundant source of fermentable sugars. A considerable amount of work has been carried out on this route to provide material for yeast fermentation to ethanol. As discussed above these wood derived sugars would also be suitable as feed for the bacterial fermentation to CMA.

Acid hydrolysis of wood has been studied for many years but it was reported at the 10th Symposium on Biotechnology in April 88 that "acid hydrolysis of wood is still uneconomical due to the high acid recovery costs", however work is continuing.

Interest has recently revived in the saccharification of wood with hydrogen fluoride (24) and the gas phase process has been studied at the pilot scale. Yields of 80-90% of D-glucose and 70-80% of D-xylose were obtained after post hydrolysis. Greater than 99% of the hydrogen fluoride can be recovered and recycled.

A recent paper (25) claims rapid hydrolysis of wood by 100% hydrogen fluoride (2 minutes at 50°C and 101.3 kPa (1 atm.)) followed by a post hydrolysis treatment with 2N trifluoroacetic acid. A 90-94% theoretical yield of glucose is claimed from Big Toothed Aspen ground wood. Although this is encouraging this would be a difficult process to adapt to the commercial scale and the handling of a large volume of hydrogen fluoride may pose environmental problems.

The alternative of using organisms with high concentrations of cellulases has been studied, particularly *Trichoderma reesi*, however its action is slow. It is inhibited by the products of breakdown, the crystallinity of the cellulose itself and the lignin in the wood (26). At the present time, it does not appear to be economic to biologically treat wood to obtain glucose.

4.6/ CMA from Cellulosic Wastes

U.S. Patent 4,430,240 (27) describes a method of preparing a mixture of the calcium salts of acetic, lactic and glycolic acid from sawdust or newsprint. The raw material is presoaked with approximately 1% sulphuric acid then neutralized with excess calcium hydroxide and treated at

about 300°C under pressure for 3 hours. A yield of impure salts of around 40% on dry sawdust weight which is useful as a deicer is claimed. The process sequence is shown diagrammatically in Figure 5. Using the concept of carbon efficiency developed for process comparison, a value of only 27.5% is estimated for this case. Use of this crude acid mixture as a deicer would require further testing. It is doubtful that it would be as efficient as pure CMA, the solubilities of the calcium and magnesium salts of glycolic and lactic acid in cold water are very much less than the solubilities of calcium and magnesium acetates.

Because both of the previously mentioned routes use wood as the basic carbon source they are not selective for acetic acid. They therefore require excessive volumes of feedstock and produce large volumes of by-products. These by-products must be sold or otherwise disposed of.

4.7/ Pyrolysis of MSW and Biomass

An alternate approach to utilizing renewable resources is to convert the material to syngas (CO and H₂) by oxidative pyrolysis and then use conventional processes to produce acetic acid from the syngas. This approach has merit and a more detailed economic assessment is given in Section 3 (Process Assessment).

5/ Newer Chemical Routes to Acetic Acid/CMA

The preferred methods for the preparation of acetic acid have undergone several changes in the last 50 years and alternatives to the current technology are still actively being sought.

5.1/ Direct Oxidation of Ethylene

Acetaldehyde used for acetic acid production (see Section 2.2) is usually prepared by air oxidation of ethylene. A logical step would be combining these two steps and this has been investigated. (The earlier method of hydration of acetylene to acetaldehyde is now obsolete).

Palladium based catalysts are used to oxidize acetaldehyde to acetic acid (28). When combined with vanadium pentoxide, this type of catalyst oxidizes ethylene with 50% selectivity to acetic acid. This liquid-phase ethylene oxidation using palladium chloride and vanadium compounds is enhanced further by the presence of sulfate (29). Sulfate also modifies and improves the activity of the palladium-gold alloy catalyst for vapor-phase ethylene oxidation (30). In the presence of sulfate, selectivities of ethylene to acetic acid of the order of 85% have been reported. In its absence, almost all the ethylene is converted directly to carbon dioxide. The relatively high cost of ethylene will prevent commercialization of this route.

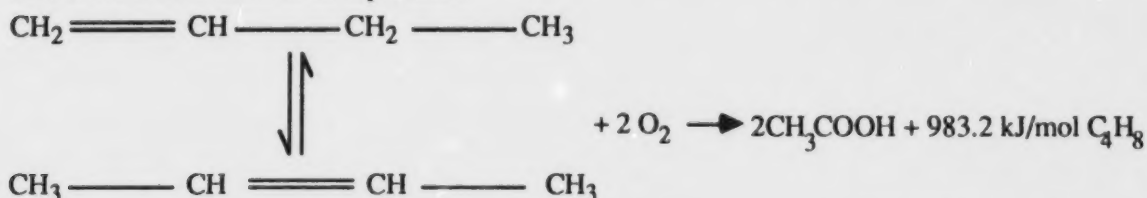
5.2/ Propylene Oxidation

Propylene may be oxidized at high temperatures to acetic acid but acrolein, acrylic acid and other compounds are significant coproducts (31). Vanadium pentoxide and tungsten trioxide mixtures with tin oxide or molybdenum oxide are favoured as catalysts. Acetic acid can be recovered from the crude gases by absorption in diethyl phthalate at 65 - 70°C, then entrainment in a current of nitrogen at 90°C. Acrylic acid remains dissolved in the solvent.

Details on yields and selectivities are not given. It does not appear to be a viable route to acetic acid for CMA. Some other cheaper means would have to be found to remove the acrylic acid impurity and a market for the acrylic acid or its derivatives found. Simple hydrogenation would give propionic acid as a major impurity in the acetic acid. It would probably pass through as calcium/magnesium propionate impurity in CMA.

5.3/ Butenes Oxidation

The butenes, which are significant coproducts in ethylene production, particularly when naphthas are being cracked, are attractive raw materials for acetic acid manufacture. Because of the mobile equilibrium between butene-1 and butene-2 under the reaction conditions, the mixture of the isomers can be used without separation.



In theory, 1 kg of butene will yield 2.14 kg acetic acid. Temperatures of 200 - 320°C are required more particularly 240 - 275°C (32). Catalysts containing vanadium oxides, along with a variety of other oxides, are used. Titanium, zinc, aluminum, or antimony oxides have been mentioned. The specific surface area of the catalyst may vary from 20 to 200 m²/g. Careful selection and preparation of the mixed oxide catalyst is essential. For example, titanium-vanadium oxide mixtures direct the reaction to maleic anhydride rather than acetic acid, whilst vanadium pentoxide on an aluminum oxide carrier leads unselectively to a mixture of acids, aldehydes, and ketones. Only the correct combination of oxides will provide the high selectivity to acetic acid desired.

Butene oxidation operating conditions are as significant as the catalyst to the process. A large excess of oxygen, generally 3 - 6 mol/mol of butene, is used to ensure complete conversion of the olefin. Steam, from 30 to 50 vol.%, is added to improve the selectivity to acetic acid although it slows the reaction. More steam could be added but it is normally kept low in order to avoid the need for later acid concentration. The lower limit, about 30 vol.%, represents the level at which selectivity is impaired.

Uniform mixing is obtained with a fluidized catalyst bed operated at 200 - 500 kPa (2 - 5 atm.). If a fixed-bed catalyst is used, pressures of 1500 - 3000 kPa (15 - 30 atm.) are needed. Space velocities of 1800 - 3600 h⁻¹ are necessary. The hourly yield of acetic acid is about 200 g/l of catalyst. Conversions are between 60 - 90%. The coproducts are mainly formic acid and maleic acid, with lesser amounts of propionic acid, acrylic acid, and formaldehyde. Traces of acetaldehyde, isopropyl alcohol, acetone, butyl acetate, sec-butyl alcohol, and oxides of carbon are also found. The separation problems are similar to those involved in purification of butane liquid-phase oxidation products (see Section 2.3).

Butenes are intermediate products in both petroleum refining and basic petrochemical operations. The majority of butenes are used to produce high quality gasoline blending components for non-leaded gasoline while petrochemical usage includes butadiene, secondary butanol, maleic anhydride, butylene oxide and polymer production. It is unlikely that CMA production from butenes could compete economically with these present uses.

A minor variation of butene oxidation is to initially react the butenes with acetic acid to give sec-butyl acetate then oxidize this ester with air (33). The limitations listed above still apply, however, and a further processing step has been introduced.

5.4/ Carbonylation of Methanol

The current carbonylation technology is based on the use of a homogeneous rhodium catalyst. Alternative to rhodium and the use of heterogeneous catalysts have been studied. A review of the possible catalysts is given in "Methanol et Carbonylation" (34).

a) Homogeneous Catalyst

This review compares the current rhodium based process with alternatives using nickel, cobalt, iridium, ruthenium, etc. The search for alternatives is driven by the high price of rhodium.

i) Nickel

This system gives quite an effective catalyst but does tend to promote the formation of by-product methane from the methanol. A minor problem but not a serious drawback unless it becomes excessive. The principal reason which has limited the utility of this system is the high pressure required; an order of magnitude greater than required for the rhodium catalyst.

In the last decade Halcon (35,36), Mitsubishi Gas (37) and Rhone-Poulenc (38) have all attempted to overcome this problem by the use of promoters, amines, phosphines or salts of lithium, sodium, potassium, chromium or vanadium. Some success was achieved with respectable operation at around 150-200°C and 6-7 MPa (60-70 atm.). Good production rates up to 500 g/h⁻¹ are reported. However, although the general mechanism is quite similar to the rhodium catalyst, the catalyst does require promoters and by-products do pose a problem. In addition, separation and recycling of Ni (CO)₄ is a problem because of its volatility, also the nickel is susceptible to oxidation by impurities in the gas or acetic acid which necessitates working in the presence of hydrogen. A process based on this catalyst

would require further development work and would be more difficult to operate to maintain satisfactory performance than the rhodium.

ii) Cobalt

Cobalt was used by BASF many years ago but was replaced by the rhodium process however it is still receiving attention in the laboratory. Like the nickel above, it requires a co-catalyst (39) (promoter) and a hydrogen atmosphere. The co-catalyst is platinum based. Pressures required are high (approx. 20 MPa (200 atm.)) and methane and other by-products of hydrocarbonylation are formed.

iii) Ruthenium

This is an active catalyst for methanol carbonylation but requires a higher temperature, 200-220°C, and a higher pressure, 30 MPa (300 atm.) than rhodium. It can also be operated in the gas phase. Selectivities up to 99% and rates around 400 g/h⁻¹ have been reported. However there is a tendency to form higher acids (propionic, etc.) which limits the utility of the system. A mechanism analogous to the rhodium case has been proposed (40).

iv) Iridium

This has also been found to be the basis of an active catalyst but the mechanism is apparently much more complex (41). Control of by-products would therefore be expected to be difficult. Relatively little work has been reported on this system and it appears unlikely to form the basis of a satisfactory catalyst.

b) Heterogeneous Catalysts

The current carbonylation process uses homogeneous catalyst systems which give good controlled reaction conditions but catalyst recovery and recycle is complex and expensive. This expense could be avoided if a good heterogeneous (fixed bed) catalyst could be used. Several attempts have been reported using zeolites, carbon and synthetic resins to support rhodium and other potential catalysts.

i) Rhodium on Zeolites

The Japanese (42) have studied the vapour phase reaction using a Rh-Y zeolite catalyst at 155-200°C. The product, however, was methyl acetate because no water was introduced to their system. The reaction mechanism was found to be very similar to the homogeneous rhodium complex catalyst, 1st order in methyl iodide, zero order in methanol and carbon monoxide.

Recent German work (43), again in the vapour phase using Faujasite-Type Zeolites has shown the carbonylation activity to be strongly dependent on the Si/Al ratio with a maximum at Si/Al = 1.3-1.5.

Although both these studies are on the laboratory scale the data obtained suggests that development to a commercial scale may be possible. Further work is required to prevent or utilize methyl acetate production.

ii) Rhodium on Resins

Rhodium deposited on a variety of synthetic resins has been studied (44) for the methanol carbonylation in the presence of methyl iodide. All work was at low pressure and between 100 and 200°C. The highest activity was observed with a rhodium exchanged Na-Amberlyst 15 sulphonic acid ion exchange resin. Methyl acetate was produced with 82.5% selectivity. Acetic acid was not produced principally because water was not introduced to the system. Again, development along these lines may result in a good acetic acid catalyst.

iii) Group VIII Metals on Carbon

Nickel on carbon has been evaluated in the presence of a variety of salts (45). Good activity is claimed 280-320°C, 100-1000 kPa (1-10 atm.) giving 280-400 g/h⁻¹, however excess methane is produced as by-product. Nickel on silica or alumina are also reported to be effective but both require much higher pressures.

Nickel, rhodium, palladium, iridium, cobalt and ruthenium have all been studied for the vapour phase carbonylation (46). It is apparent that with an active carbon support at 300°C 99% methanol conversion is achieved with 95% selectivity to acetic acid. The by-products are methyl acetate, dimethyl ether and methane. The rhodium based system shows the highest activity at the lowest temperature although a practical catalyst based on nickel or iridium may be possible.

5.5/ Acetic Acid from Syngas

a) Isomerization of Methyl Formate

Acetic acid is an isomer of methyl formate, which, like methanol, can be produced from carbon monoxide and hydrogen (6). Methanol reacts with synthesis gas at 80°C and pressures of 10 MPa (100 atm.) or higher in the presence of potassium methoxide as a catalyst to give the methyl formate. The mole ratio of carbon monoxide to hydrogen is maintained at about 2:1.

Methyl formate may be isomerized over a catalyst composed of hydrofluoric acid on carbon, or a complex rhodium triphenylphosphine carbonyl in the presence of a methyl iodide promoter to give the acetic acid.

b) Direct Synthesis from "Syngas"

Claims are made for the direct synthesis without the isolation of either methanol or methyl formate (6).

Using essentially the same catalyst for methyl formate isomerization, rhodium triphenylphosphine carbonyl, but at more severe operating conditions significant quantities of acetic anhydride are produced. A modification of this system, obtained by depositing rhodium chloride onto silica gel, drying and reducing in hydrogen, has shown good activity for acetic acid production at 250°C and approx. 18 MPa (175 atm.) using a 3:1 (CO:H₂) syngas. Expensive metallurgy was required, however, and cheaper materials would have to be developed for an economic process.

Other systems have been tried in the laboratory (47), the ruthenium "melt" catalyst is claimed to give >80% selectivity to acetic acid. This system requires cobalt iodide as a co-catalyst and a tertiary phosphonium halide, typically tetrabutyl phosphonium bromide. Reaction conditions are around 49 MPa (480 atm.) at 220°C. Even under these forcing conditions the reaction is quite slow and methyl acetate, ethyl acetate, methanol and ethanol are produced as by-products. The active component of the catalyst system appears to be a ruthenium carbonyl iodide. Big improvements in the total system, a more efficient catalyst operating at a lower pressure, will be required if this method is to replace the carbonylation of methanol process with the rhodium catalyst.

5.6/ Direct Synthesis from Methane

The direct oxidative coupling of methane and oxygen to produce acetic acid has not been reported.



The usual result of attempts at this reaction are carbon dioxide, ethylene and ethane. This reaction is documented in a recent series of papers (48). Most reported catalysts are alkali promoted oxides. Under more selective conditions, carbon monoxide can be recovered as a product (49). In one recent study, the direct conversion of methane to methanol is reported (50). At around 420°C with 2.8% oxygen in methane and 3.5 MPa (35 atm.) around 5.8% methane conversion was found with 77% selectivity to methanol. This methanol could be used for carbonylation, the by-product was carbon monoxide. Methanol and carbon monoxide were produced in approximately equal molar amounts (the ratio required for carbonylation) when the oxygen content of the feed was increased to 5.2 - 8.0%. If this reaction could be satisfactorily scaled up it would give a good route to a methanol carbonylation feed.

5.7/ Acetic Acid from Methane and Carbon Monoxide

It is reported that under very strongly acidic conditions (superacids) that methane can react with carbon monoxide to give an acetyl cation. This cation reacts with water to give acetic acid (51).



A similar type of reaction has been observed when alkanes (methane) are submitted to electrochemical oxidation in fluorosulphonic acids (52). Although this route appears a relatively efficient route to acetic acid, there would undoubtedly be problems in scaling it up to a commercial scale. "Superacids" are expensive and very reactive, hence they would have to be very efficient and selective catalysts.

5.8/ Acetaldehyde from Methane and Carbon Monoxide

Syngas can be absorbed onto the surface of magnesium oxide previously heated at 1100°C in a vacuum. In the temperature range of 70-310°C they react to form formaldehyde (53). At higher temperatures methanol was detected. There is also evidence that the C-H bond in alkanes can be cleaved on similar surfaces, hence subsequent reaction with carbon monoxide would lead to acetaldehyde. This can be oxidized to acetic acid.

6/ Availability of Raw Materials and Plant Location

The assumption of the availability of sufficient raw materials at the assumed price is built into the economic studies. All processes are designed to use natural gas as fuel and it is also used as a feedstock for the base case and the processes based on MSW and wood. The economic supply of this and dolostone are essential for the manufacture of CMA.

6.1/ Natural Gas

This is produced in Ontario, principally in South Western Ontario and from Lake Erie. Installed gas treating capacity is $1.239 \times 10^6 \text{ m}^3/\text{d}$. This is equivalent to only 62% of the requirement for the base case, but is more than sufficient for the processes based on MSW and wood (demand = $0.54 \times 10^6 \text{ m}^3/\text{d}$). The case based on corn fermentation is calculated to require $1.5 \times 10^6 \text{ m}^3/\text{d}$, in excess of the Ontario supply, principally because of the need to evaporate large amounts of water.

Although natural gas is produced in the province it is not available as a segregated resource but is blended with Western Canadian gas in the gas distribution system.

It will be more practical to, in fact, take the required gas from Alberta. The demand for natural gas for any of the proposed methods is sufficiently great that long term supply contracts with Western Canadian producers and Trans Canada Pipelines should be negotiable. This need for a large supply of natural gas affects the choice of a plant site in so far as it should be reasonably close to the trunk pipeline.

6.2/ Alternative Fuels

Alternative fuels could be used to provide the energy, however these have not been considered because of overall cost. Coal could be imported, probably from the U.S., at a reasonable cost on an energy content basis, however this fuel would require more expensive handling, more expensive boilers and require flue gas clean up equipment to be installed.

Electricity is too expensive and is not used for providing chemical process energy. It is a secondary energy source being obtained by converting the primary energy source natural gas, coal, oil, hydro or nuclear.

6.3/ Calcium and Magnesium Source

The prime source of the calcium and magnesium will be dolostone which is widely distributed throughout Ontario. In spite of this the actual locations where it has the required high magnesium content and can be economically extracted and transported are quite limited. The potential availability and limitation are discussed (54).

CMA manufacture requires a dolostone with a high content of Mg. Typically, dolostones will have a range of 11-21% MgO and 44-30% CaO. A relatively pure dolostone such as that found in the Nelson Quarry forming the Niagara Escarpment would have MgO = 21% and CaO = 30% with about 2% impurities (silica and clay). If all CaO and MgO is dissolved in the process, the Ca/Mg mole ratio = 1.02. It is not possible to achieve lower ratios unless there is either addition of extra MgO or selective dissolution of MgO. (Not all CaO goes into solution). The purer the dolostone the less the processing required to give a high quality CMA.

a) Potential Sources in Ontario

There are a number of dolostone formations in Ontario which have the potential of providing dolostone of the appropriate quality:

Map No. (Figure 6)

- 16 *Detroit River Group*: especially the Lucas Formation found in the Woodstock area. There are existing quarries and the good sites (low overburden) are mainly developed. Poor prospect.
- 13 *Bertie Formation*: found in outcrops from Hagersville to Fort Erie. To the northwest of Hagersville, the overburden is probably too thick for economic exploitation. Generally the formation is very likely to be too thin or impure as a source of raw feed for CMA. Poor prospect.
- 12 *Salina Formation*: This runs in a broad band from Niagara Falls to Southampton. It is known to contain dolostone, gypsum, halite and shale. The overburden is probably too thick for quarry exploitation. Poor prospect.
- 3 *Beekmantown Group*: extensively quarried in eastern Ontario between St. Lawrence and Ottawa Rivers. Ontario government owns extensive property underlain by this rock near Morrisburg. Typical chemical analyses for rock at Iroquois (120 m thick) MgO 14-18%, CaO 21-27% and insoluble residue (quartz, clay, etc.) approx. 10-15%. A reasonable

prospect (land cheap, rural area, good infrastructure, etc.) but the high level of impurities will require extra rock to be handled, more expensive processing and disposal of the segregated impurities.

High purity dolostone will minimize processing and handling costs but reserves in Ontario are limited to the following formations:

Map No.

- 11 *Guelph Formation:* from Niagara Falls to Bruce Peninsula.
- 10 *Lockport and Amabel Formations:* from Niagara Falls to Bruce Peninsula and Manitoulin Island.

Guelph dolostone typically has $MgO = 20-21\%$, $CaO = 30-31\%$, and low insolubles (less than 3%). It has been quarried for chemical use in the Guelph-Hespeler area where extensive deposits are found (probably over 50 m). It is usually too soft for use as a construction aggregate. An excellent prospect. Samples were evaluated for dissolution in glacial acetic acid and were superior to the Amabel dolostones.

The Lockport and Amabel Formations have similar chemistry to the Guelph, and are strong enough to be used for construction aggregates. They suffer from the disadvantage of usually being in the Niagara Escarpment area where development of this nature is severely restricted. Amabel is quarried in a very large deposit (with deep water shipping) at the west end of Manitoulin Island. Typically, $MgO = 21\%$, $CaO = 30\%$, and insolubles less than 2%. Of all the Amabel outcrops, this is the best prospect but lacks significant infrastructure. Manitoulin dolostone is currently available at a cost of about \$6-7 per tonne delivered to any deep water dock on the upper Great Lakes (above Welland Canal).

Extraction of Guelph and Amabel rock from a deep mine (200-1000 m) anywhere to the south and west of the outcrop area should not be discounted. CMA has a relatively high value; the cost of mining compared to quarrying may not necessarily have a major influence on cost.

Four possible target areas which could provide a long term secure supply of the appropriate quality dolostone are:

- a) Existing quarries in the upper Great Lakes, e.g. Standard Aggregate Manitoulin Island with costs controlled by long term supply contract. Delivery to manufacturing facility close to deep water port.
- b) Develop a new quarry close to a deep water dock, but sites are limited.
- c) Develop a new quarry in the Guelph or Amabel formation in Southern Ontario away from sensitive areas. Processing on site would be desirable.
- d) Establish a deep mine in the Guelph or Amabel again in Southern Ontario and close to plant site.
- e) Purchase dolostone from a number of existing producers.

All the above have points from and against, which must be considered with other factors when selecting the best overall option.

6.4/ Municipal Solid Waste

It is estimated that 0.727 tonnes of suitable MSW are produced per capita per year. This includes most of the residential waste and about 50% of the commercial and industrial waste. A 1 MT/a CMA plant requires around 6000 tonnes/day of raw MSW. This amount is only available in the greater Metro Toronto region. Hence any plant based on utilizing this resource would best be sited close to or within economic trucking (or rail) distance of Toronto. If this must be trucked it would probably be desirable to site the plant at the dolostone source. The alternative of bringing the dolostone to the MSW source should also be considered; dolostone required is only 30% of the MSW weight.

Other organic waste could be used to supplement MSW, e.g. Agricultural wastes and tires.

6.5/ Wood

This is a more diffuse resource than MSW and the necessity to minimize costs would limit this to wood of no other economic value. This would generally mean slash and other timber waste

normally left in the bush. This could be had presumably for the cost of collection and delivery. Wood transport is normally about \$2/tonne mile. Providing enough material, 4320 tonnes/day, would require collection over a very wide area which could mean average delivered costs in excess of the \$60/tonne used for the costing.

The required amount of waste wood is estimated to exist in Ontario in the area from south of Nipissing and East of Highway 400. Additional wood is available further north but collection costs would be excessive. Supplies could also be obtained from Quebec and New York State.

6.6/ Lignite

Although no costing involving this type of resource was carried out a significant supply of lignite exists at Onakawana about 90 km south of Moosonee. Estimated reserves are 1.8×10^8 tonnes. Such a material could in theory, be used in a similar gasifier to produce a syngas. This resource is not easily transportable, it contains a high percentage of water and easily liquifies. It would have to be used on site. Earlier government studies on making methanol on site showed this to be uneconomic. It could not therefore be a basic raw material for CMA.

6.7/ Corn

Corn has been proposed as a source of fermentable sugars for CMA. The economic evaluation shows a very large demand for corn for a 1 Mt/a. CMA plant around 8500 bushels/hour. The effect of this level of demand on the Ontario corn production is illustrated in Table 4, over the last four crop years this amounts to 29 to 45% of the total production. Note production is seasonal but consumption is not, hence storage of large quantities will be required. The good corn growing area is in extreme South Western Ontario, yields decrease to the north and east of this prime area. Apparently there is limited scope for increasing the amount of corn grown, the present tobacco farm land is unsuitable for corn. The best corn yield in Ontario is well below the prime areas in the U.S.

Utilizing Ontario corn for CMA would put a sufficient demand on the market to affect prices, which would please the farmers, but make CMA prohibitively expensive.

6.8/ Lime

Lime is required for the fermentation method for CMA and is also used with the acetic acid procedures. For the base case, and the alternative dolostone dissolver option, the liberated carbon dioxide from the dolostone is utilized to make syngas and the lime must be made on-site. Dolime is commercially available and could be purchased, the fermentation method assumes purchase rather than on site production. Dolime is currently produced by Steetley in Dundas and by Guelph Dolime.

The liberated carbon dioxide is not required for the fermentation or MSW/Wood cases and dolime could be used.

6.9/ Externally Produced Methanol and Acetic Acid

The chemical methods of producing CMA all have methanol and acetic acid as intermediate products. Any external source of these intermediates could be used to supplement the main production. Thus minor amounts of dilute acetic acid could be used but the price to the suppliers would have to be comparable to its worth in the process. A similar situation could exist for methanol streams. Surplus methanol from Western Canada or offshore could be accommodated. Product qualities would also have to be comparable with the plant products. This flexibility would allow small producers of the chemicals to market their production from biomass or other sources if they can do it economically.

6.10/ Plant Locations

a) Natural Gas Feedstock

It would appear that a location would preferably have:

- Access to Western Canada Natural Gas via the trunk pipe.
- Access to dolostone either on site or deliverable cheaply.
- Good access to water transportation either for dolostone receipt or product distribution or both.
- Good infrastructure, power and skilled labour force.
- Sufficiently close to major markets that transportation costs are not excessive.

Given these criteria a location in the Sarnia area is probably optimum. The dolostone could be supplied from Manitoulin by ship and much of the product distributed by ship.

Other locations in South Western Ontario could also be considered.

b) MSW Feedstock

If this feedstock is chosen then the plant would preferably be located:

- Within economic trucking distance of the major MSW supply (Toronto Region).
- Access to dolostone either on site or deliverable cheaply.
- Good access to water transportation.
- Good infrastructure.
- Access to good natural gas supply.

Not all these criteria could be satisfied. Ideally sites in the Niagara area with access to water or the Guelph/Hespeler area would probably be the best compromise. The feasibility of a site close to the MSW supply should also be considered.

c) Wood Feedstock

This is generally less economic. Siting to minimize the cost of delivered wood would be necessary. Sites in the Georgian Bay area, allowing Manitoulin dolostone to be used, or perhaps Eastern Ontario may be possible. A very thorough economic study would have to be undertaken to site this option optimally.

d) Corn Fermentation

A location in the prime corn growing area with access to water would be required within an economic distance of a dolime plant. A deep water dock on Lake Erie would probably be the location of choice. Good access to natural gas would be required.

Process Assessment

1/ Introduction

On the basis of the technology review, it is obvious that a process, or in fact, a series of processes, to produce a large volume of CMA has not been tested commercially. The choice, therefore, appears to be between producing acetic acid and reacting with a calcium and magnesium source to produce CMA, or the direct production of CMA by producing "acetate" in the presence of calcium and magnesium ions.

This assessment considers three basic production scenarios:

- 1) Manufacturing of acetic acid at the lowest possible cost followed by reaction with dolime (base case).
- 2) Manufacture of acetic acid from renewable raw materials followed by reaction with dolime.
- 3) Manufacture of CMA from biomass fermentation.

The conclusions from this study are summarized in Table 5.

2/ CMA via Acetic Acid

2.1/ Choice of Acetic Acid Route

It is concluded that methanol carbonylation is the preferred process for acetic acid manufacture. Although comparative economic data, i.e. a direct comparison with rival processes done for the same site at the same time, are difficult to find, SRI have published a comparison between the acetaldehyde oxidation and the methanol carbonylation (55).

Major Cost Components of Synthetic Acetic Acid Manufacture

	Acetaldehyde by Oxidation with Air		Low Pressure Carbonylation of Methanol	
	Cents/lb.	Cents/kg	Cents/lb.	Cents/ kg
Net Variable Costs	23.2	51.5	8.54	18.8
Raw Materials	20.3	44.8	6.61	14.6
Utilities	3.7	8.2	1.93	4.2
By Product Credits/(Debits)	-0.9	-1.9	-	-
Labor	0.3	0.7	0.42	0.9
Other Production Costs	2.2	4.8	2.75	6.1
Total Production Costs	25.7	56.6	11.71	25.8
Canadian Cents	38.2	84.2	17.4	38.4
Canadian \$/tonne		842.1		383.7

These data were generated in mid 1984 U.S. dollars. The final lines in the table are calculated to current Canadian dollars by assuming inflation at 5% and U.S. \$ = 1.2225 Cdn. \$.

From these data it is obvious why methanol carbonylation is the choice for new plants over the acetaldehyde oxidation. Unfortunately similar data for the n-butane oxidation route are not available in this article. It is stated, however, that "production costs are now high because the n-butane process is very energy intensive".

From the previous table, it can be seen that raw material costs are the major difference between the two processes. Labour and "other production" costs are slightly lower for the oxidation route. The value shown in Canadian dollars should be considered for comparison only, the full basis of

the SRI estimate is not known; financing arrangements, taxes, labour rates, insurance and interest rates would all be expected to be different from the Ontario situation. Nonetheless the value of \$ Cdn. 384/tonne for acetic acid from methanol suggests that a net production cost for CMA of less than \$ Cdn. 350/tonne would be possible because dolomitic lime is inexpensive.

2.2/ Calcium Magnesium Acetate (CMA) Manufacture

The production of CMA from acetic acid is not a large scale commercial process (Chevron operate a small plant but there were no economic data available). In order to do a meaningful economic assessment therefore, the drum pelletizer process of Gancy (56) was selected because of its projected lower costs (21.5 cents/lb.) than the SRI process (27.3 cents/lb.) based on a fixed price for glacial acetic acid of 25 cents/lb. In both processes, the calcium and magnesium are provided by purchased dolomitic lime.

Assumptions made in the evaluation are that the calcium magnesium molar ratio = 1 and that the product is the hemi hydrate $\text{CaMg}(\text{CH}_3\text{COO})_4 \cdot 0.5\text{H}_2\text{O}$ in line with the Gancy report (56), i.e. not completely anhydrous.

2.3/ Base Case - Natural Gas - Methanol - Acetic Acid - CMA

The combination of acetic acid by methanol carbonylation and subsequent reaction with dolomitic lime by the above Gancy process was selected as the base case for economic evaluations. Details of the evaluation are given in Appendix I.

Because of the large plant size, the purchase of merchant methanol was not considered. Instead this economic evaluation assumes natural gas (methane) as the basic raw material, with additional "carbon" being supplied from the production of lime and recovery of carbon dioxide from flue gases. The natural gas to be supplied by pipeline from Alberta at a contract price of \$2.42/GJ (\$2.55/1000 SCF).

The process described in Appendix I combines proven commercial units. Natural gas is reacted with CO_2 , extracted from the lime plant and flue gases, and steam in a reformer to produce syngas. After extracting a portion of the CO, the syngas is converted to methanol which reacts with the excess CO to produce acetic acid. This in turn reacts with dolomitic lime to produce granular CMA.

Table 6/ Natural Gas - Methanol - Acetic Acid - CMA

	\$/tonne CMA
Feedstocks and Utilities	75.33
Catalyst and Chemicals	2.80
Labor including Supervision, etc.	1.18
Maintenance	16.34
Insurance, Taxes & Overheads	29.04
Royalties	<u>3.00</u>
Sub-Total	137.68
Contingency (10%)	<u>13.77</u>
Total Operating Cost	151.44
Interest (@ 11% on TCI)	96.80
Depreciation (7.5% on FI)	<u>54.45</u>
Total Production Cost	302.69

Total Fixed Investment = \$726 MM including 35% contingency.

a) Process Integration

This process scheme represents an integrated on-site approach to CMA synthesis with by-products and off gases being recycled to other units. This is possible because methane, carbon monoxide and carbon dioxide and lime are the basic raw materials. Such close integration would not be possible with either the acetaldehyde or the n-butane oxidation routes. The use of by-product carbon dioxide significantly reduces natural gas requirements and hence feedstock costs.

As summarized in Table 6, using this approach it may be possible to manufacture CMA for \$300/tonne. Details of the assumptions used in this assessment are given in Appendix I.

Although this base case process is optimized on current technology, improvements may be possible which would further improve the economics. For example, impure aqueous acid is potentially available as an intermediate stream in the process. It is likely that such a stream could be used to make CMA of sufficient purity for deicing. This excess water is currently removed by evaporation (heat) to produce the glacial acetic acid which is subsequently diluted with water again to react with lime then the added water re-evaporated.

Utilizing the intermediate acid stream will reduce the capital and operating costs for the acetic acid unit. The estimate does not include this cost saving, to obtain a good estimate a more detailed review with the process licensor would be required.

Little information is available on the direct reaction of acetic acid with limestone. If this could be achieved further significant capital and operating savings could be made. Effectively the lime plant and CMA plant could be combined into one unit.

3/ CMA from Alternative Raw Materials

While under current economic conditions the preferred basic raw material for the production of syngas for CMA manufacture is natural gas, other carbon sources have been considered. Eastman have used coal in their complex at Kingsport, Tennessee to produce acetic anhydride (57). In Ontario two major sources of carbon are available, MSW and wood which can be converted to syngas in a "slagging gasifier" such as a "Purox" unit developed by Union Carbide. Since the syngas produced from MSW or wood is hydrogen deficient, a natural gas reformer can be used to produce hydrogen rich syngas to supplement the Purox unit output.

This hybrid approach of producing a balanced syngas for acetic acid manufacture was used to generate the values shown in Table 7. The details of the process design and economic assessment are given in Appendix II.

Table 7/ MSW/Wood - Methanol - Acetic Acid - CMA

	\$/tonne CMA	
	MSW*	WOOD
Feedstock and Utilities	42.93	128.19
Catalyst and Chemicals	1.64	1.64
Labor including Supervision, etc	20.29	20.29
Maintenance	22.93	21.08
Insurance, Taxes and Overheads	40.76	37.40
Royalties	<u>3.50</u>	<u>3.50</u>
Sub-Total	132.06	212.18
Contingency (10%)	<u>13.21</u>	<u>21.22</u>
Total Operating Cost	145.26	233.40
Interest (@ 11% on TCI)	134.53	123.86
Depreciation (7.5% on FI)	<u>76.43</u>	<u>70.28</u>
Total Production Cost	356.22	427.54
Credit for Recovered Materials	15.39	0.00
Net Production Cost	<u>340.83</u>	<u>427.54</u>
Total Fixed Investment (35% Contingency)	\$1019 MM	\$937 MM

* Assumes a "tipping fee" of \$30 per tonne.

Production of CMA from MSW has certain advantages. It would significantly reduce the volume of MSW in Southern Ontario. In addition, producing syngas from both MSW and natural gas provides flexibility for handling changes in MSW availability and composition.

The major disadvantages of this approach are:

- It is more expensive than the base case natural gas route.
- The availability and reliability of large scale gasification technology needs confirmation.

The economics of this MSW scheme are very dependent on the tipping fee it is possible to charge. A tipping fee of \$50/tonne would reduce the production cost to \$305/tonne.

Table 7 also shows the economic data for the case where waste wood is used in the same process set up to replace MSW. The capital costs are reduced but this is more than offset by the cost of the wood raw material at the plant gate.

4/ Fermentation of Corn

SRI, the University of Georgia and New York State Energy Research and Development Authority have all considered the bacterial production of acetate in the presence of calcium and magnesium ion as discussed in the technology review. SRI and the University of Georgia have provided some economic projections based on laboratory evaluations.

4.1/ SRI Evaluation (57)

This evaluation was based on a 1000 short tons/day plant using either corn grain or glucose syrup. Simple escalation of SRI's final cost to current values by assuming the 5% inflation (1982-1988) and U.S.\$ = 1.2225 Cdn. \$ gives a net production cost of \$679/tonne. However, this simple approach, fails to take account of several other factors involved in the translation to the current Ontario situation.

- The corn price is subject to market fluctuation and is generally governed by the Chicago Board of Trade market, current quotes are shown in Table 9.
- The original design called for coal fired boilers and consequent flue gas clean up. In Ontario, the boilers would be fired by natural gas which eliminates the need for flue gas treatment.
- Lime - by suitable siting in Ontario, lime would be available considerably cheaper than assumed by SRI.
- Financing was calculated by SRI assuming 100% equity with 15% DCF. The basis used here assumes bond financing at 11% interest rate.
- The plant size is increased to 1 M tonnes/year.

Incorporating these changes reduces the production cost for CMA to \$530/tonne. The cost breakdown is summarized in Table 8 and a detailed description is provided in Appendix III.

Table 8/ Corn Grain - CMA by Thermophilic Bacteria

	\$/tonne CMA
Feedstocks and Utilities	296.61
Catalyst and Chemicals	13.78
Labor including Supervision, etc.	14.90
Maintenance	15.82
Insurance, Taxes and Overheads	28.12
Royalties	<u>2.00</u>
Sub-Total	382.79
Contingency (10%)	<u>38.28</u>
Total Operating Cost	421.07
Interest (@ 11% on TCI)	93.83
Depreciation (7.5% on FI)	<u>52.73</u>
Total Production Cost	567.62
By-Product Credit (Animal Feed)	<u>(37.93)</u>
Net Production Cost	<u>529.69</u>

Total Fixed Investment = \$703 MM including 35% contingency.

The by-product animal feed was originally assumed by SRI to be worth U.S. \$200/tonne, twice the value of corn. Table 8 assumes equivalent by-product and corn prices. If SRI relative values are taken the net production cost is reduced to \$491.76.

4.2/ University of Georgia Evaluation (59)

The University of Georgia's evaluation is generally similar to the SRI above, however they concentrated on using corn syrup as the glucose source and assessed a number of different fermentor designs. A summary of their results is shown in Table 10. The data are their values in U.S. cents/lb. (1st quarter, 1985).

Accounting procedures differ from the SRI case in several aspects including an assumed 50% debt financing and an alternate method of handling depreciation.

Their best base case, with batch fermentation, gave a calculated plant gate cost for CMA of U.S. \$0.24/lb. equivalent to approximately \$750 Cdn./tonne in current dollars. Assuming the factors affecting this number are the same as the SRI case above, the revised value would be approximately \$585 Cdn. per tonne.

5/ Production of Commodity Chemicals by Fermentation - Assessment

It is well recognized that there are both operating and design problems associated with large volume fermentors especially if sterile fermentation is required.

Preventing problems due to contamination by other organisms is not difficult for small short term batch operations. It is only necessary in this case to clean thoroughly between batches and inoculate the fermentation media with a high concentration of the desired organism. In this case, the nutrients are consumed before any contaminant has an opportunity to grow to significant levels.

However, in large scale and continuous processes, prevention of contamination is very important and difficult. It would be necessary to sterilize all feeds. Peter King of ICI (60) observed that for the Pruteen process it took 3 months of minute attention to detail to overcome sterilization problems. (On the other hand, if the fermentation medium was only suitable for halophilic growth, sterility may be less of a problem).

The Pruteen plant is the largest sterile fermentation operation in the world. Its fermentor is 1500 m³ and it can make 50 000 tonnes of product per year. It cost ICI \$150 million, in the early 1980s, (61) to get it into production (albeit this does include the cost of nutritional studies). In order to operate a fermentor on this scale, ICI had to develop a new fermentor design, develop new valves, and find a new anti-foaming agent. The technology which ICI developed has been organized into a proprietary technology package which ICI offers for sale. Building a fermentor to produce a million tonnes (i.e. 20 times the capacity of the ICI plant) of a commodity chemical like CMA does not seem practical with present day technology.

6/ Specifications for CMA

The current Ontario specification for CMA is shown in Table 11. This will require some modification if it is to cover the production of CMA from native Ontarian dolostone. The specifications, as written, cover a CMA with increased magnesium content, which could only be met using the addition of a second mineral rich in magnesium, e.g. magnesium oxide derived as a by-product from seawater processing or magnesite. In principle, high magnesium contents are desirable giving slightly greater solubilities and larger freezing point depressions (but a recent study did not show any advantage in ice melting studies for the magnesium enriched CMA (62)). Some of the specifications should also be quoted in metric units.

The revised specification could be:

- Items 1 to 3: no change
- Item 4: rewritten to include metric units: Deicing Ability - melts ice at $-4^{\circ}\text{C}(25^{\circ}\text{F})$ producing 10 ml of water/h/m² (1 ml of water/hr/sq. ft.) over a 24 hour period under laboratory conditions when applied at 82 g/m² (7.6 gm/sq. ft.) of ice.
- Item 5: Calcium, magnesium, carbon and hydrogen analysis conforming to:
$$\text{Ca}_x\text{Mg}_y(\text{C}_2\text{H}_3\text{O}_2)_4 \cdot z\text{H}_2\text{O}$$

where $x = 0.6 - 1.1$
 $y = 0.9 - 1.4$
and $x + y = 2$ $z = 0 - 3$

This covers CMA from dolostone.
- Item 6: Calcium/Magnesium - The Ca/Mg molar ratio of water soluble product shall be between 0.43 and 1.22 (necessary to conform to 5 above).
- Items 7 to 10 can remain unchanged.

It would be preferable to have a further item to cover the content of acetate ion in order to limit formates, propionate and butyrates in the material. This will be covered to some extent in Item 4, but an item stating acetate to be >95% of the organic anions and butyrate <0.5% could be useful.

Items covering maximum amount of residual base may also be required, they are included in the specification for Chevron "Ice-B-Gon".

6.1/ Impurities

Trace impurities in the final CMA product will be dependent to some extent on the process of manufacture. In the product from the base case study apart from trace amounts of other organic acid salts referred to above, the impurities will be those introduced from the lime or dolostone. These, of course, will be governed by the source of the dolostone both as regards to total amount and the type. In general the concentration in the CMA will be less than in the parent dolostone even if none is removed in the manufacturing process. They would not normally be expected to pose any environmental hazard.

If CMA is derived from fermentation sources other trace minerals may appear in the product because of "carry through" of the trace nutrients. These may require further studies to determine if significant amounts are actually in the CMA and whether they pose any hazard.

The fermentation derived product is more likely to contain other organic acid salts, but all sources may have small amounts of other organic material adhering to the solid.

6.2/ Product Stability

CMA would be expected to be stable under normal ambient temperature storage at normal humidity levels. However its stability to bacteriological attack at high ambient temperature, high humidity conditions should be evaluated. It is expected that CMA will be degraded to calcium magnesium carbonate, water and carbon dioxide in the environment presumably by bacteriological action.

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TABLE 1

CLOSTRIDIUM THERMOAUTOTROPHICUM MEDIUM

Ingredient	Amount/Litre
Glucose	10 g
Yeast Extract	2 g
KH_2PO_4	1.5 g
$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$	3.1 g
Na_2SO_4	1 g
NH_4Cl	500 mg
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	180 mg
FeSO_4	5 mg
Trace Mineral Solution	5 ml
Vitamin Solution	0.5 ml
Resazurin Solution	1 ml
Reducing Solution	40 ml

Data from Reference 15

TABLE 2

**COMPOSITION OF MEDIUM FOR LARGE SCALE CMA PRODUCTION
FROM STARCH HYDROLYSATE**

Chemical	g/400 l	g/l
Hydrolyzed Corn Starch	9200*	23
Yeast Extract	2000	5
$(\text{NH}_4)_2\text{SO}_4$	400	1
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	100	0.25
$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	15.6	0.039
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	12.0	0.03
$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	1.32	0.0033
$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	0.96	0.0024
NiCl_2	0.96	0.00024
ZnSO_4	0.116	0.00029
Na_2SeO_3	0.0068	0.000017
$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$	32	0.08
Cysteine.HCl.H ₂ O	32	0.08
NaHCO_3	400	1
K_2HPO_3	700	1.75
KH_2PO_4	550	1.375

* Initial concentration of hydrolyzed corn starch. More corn starch was added to the fermentation during the run. For the total amount added see Table 3.

Data from reference 15.

TABLE 3
ANALYSES OF 400 LITRE FERMENTATIONS FOR THE PRODUCTION
OF CMA FROM CORN STARCH HYDROLYSATE

Run	Glucose (1)		Acetate Produced	Acetate (2)		Dolime (1)		Soluble (3)		Total (3)		Soluble Mg/Ca
	Added	Left		Glucose	Ratio	g		Ca	Mg	Ca	Mg	
	mm	mm	mm				mm	mm	mm	mm	mm	Ratio
1	222	41	412		2.28(2.54)	7261		48.3	146	107	145	3.02
2	250	5	393		1.60(1.80)	8864		71.0	129	135	222	1.82
3	278	5	502		1.84(2.04)	10586		58.8	168	142	179	2.86
4	278	4.3	432		1.54(1.78)	9425		54.3	144			2.65
5	250	0	403		1.61(1.81)	8275						
6	385	4	625		1.64(1.85)	11500						
7	374	25	565		1.62(1.82)	16615						
8	379	36	476		1.31(1.48)	13025						

(1) Total glucose and dolime added throughout the fermentation.

(2) Acetate/glucose ratio, was obtained by Acetate Produced
Glucose Added-Glucose Left

These values are lower than expected. However the calculations were done assuming a constant volume during the fermentation of 400 litres, whereas by addition of glucose and dolime during the fermentation the actual volume was about 450 litres. Using this volume the acetate/glucose ratios obtained are those given within parentheses.

(3) Total concentrations of Ca and Mg include both undissolved dolime suspension and dolime that has dissolved. Soluble Ca and Mg include the concentration after the undissolved dolime had been removed.

Data from reference 15.

TABLE 4

ONTARIO - CORN AVAILABILITY AND REQUIREMENTS

Year	PRODUCTION		REQUIRED FOR CMA % Production	PRICE	
	BusheIs x 10 ³	Tonnes x 10 ³		/tonne \$	/bushel \$
1985	228,400	5 801.5	29.2	113	2.87
1986	188,029	4 776.4	35.5	88	2.24
1987	215,000	5 461.0	31.1	102(a)	2.60(a)
1988(a)	147,000	3 734.0	45.4	137(b)	3.49(b)

-53-

(a) Estimate

(b) October 1st CBOT Dec. '88 delivery

TABLE 5

Options for the Manufacture of one million tonnes/year
Calcium Magnesium Acetate in Ontario

<u>Route</u>	<u>Chemical</u>		<u>Fermentation</u>
Principle Feedstock	Natural Gas	MSW/Biomass	Corn
Capital cost estimate \$MM	538	755/694	521
Proven Processes & capital cost	94	46/51	25
Process requiring scale-up	CMA 2 - 126 t/hr	CMA 2 - 126 t/hr	Fermentation Pilot Scale - 126 t/hr
Outstanding issues	Acetic Acid Licence. CMA Integration	Acetic Acid Licence, CMA Integration MSW Availability & Composition. Gasification technology availability Gasification 10 - 200t/hr.	Feasibility of pilot scale fermentation.
% Carbon utilization as CMA	71.8	54.8	28.7
Production \$/tonne	303	341/428	530
Spin-off	none	Reduces volume of MSW	Utilizes excess corn

TABLE 9
CHICAGO BOARD OF TRADE CORN GRAIN FUTURES
(OCTOBER 1, 1988)
(\$/BUSHEL)

PRICE (RANGE)				DELIVERY DATE	PRICE (CLOSE)	
High U.S. \$	Cdn. \$	Low U.S. \$	Cdn. \$		U.S. \$	Cdn. \$
3.70	4.52	1.8525	2.26	Dec. 88	2.855	3.49
3.77	4.61	1.9925	2.44	Mar. 89	2.91	3.56
3.69	4.51	2.075	2.54	May 89	2.93	3.58
3.60	4.40	2.33	2.85	July 89	2.9125	3.56
3.1775	3.88	2.45	3.00	Sep. 89	2.72	3.33
2.95	3.61	2.35	2.87	Dec. 89	2.59	3.17

Canadian prices calculated by U.S. x 1.2225

TABLE 10
UNIVERSITY OF GEORGIA EVALUATIONS
REQUIRED PLANT-GATE CMA PRICES FOR FOUR FERMENTATION PROCESSES

Cost Parameters	CMA Prices (\$ per pound) Fermentation Processes		
	Continuous	Continuous with Cell Recycling	Batch
Glucose Cost			
\$0.10/lb	0.369	0.249	0.219
\$0.12/lb*	0.391	0.271	0.240
\$0.15/lb	0.423	0.303	0.272
PFI Factor			
0.75	0.365	0.254	0.225
1.00*	0.391	0.271	0.240
1.25	0.416	0.288	0.256
1.50	0.431	0.304	0.271
Percent Equity Financing			
50*	0.391	0.271	0.240
100	0.419	0.289	0.257
Annual Operating Cost Factor			
0.90	0.358	0.248	0.220
1.00*	0.391	0.271	0.240
1.10	0.423	0.294	0.261

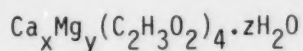
* Base analysis parameter values
Data from reference 15.

TABLE 11

SPECIFICATIONS FOR CMA

Production grade CMA shall have the following properties:-

1. Shape - CMA shall have an approximately isodimensional particle shape.
2. Size and Gradation - CMA shall have a size gradation meeting that for a Type 1, Grade 1 material in ASTM D 632 (rock salt).
3. pH 0 An aqueous solution of 10 percent CMA shall have a pH of 8-9.
4. Deicing Ability - Melts ice at 25°F producing 1 ml of water/hr/sq ft over a 24 hr period under laboratory conditions when applied at 7.6 gm/sq ft of ice.
5. Calcium, magnesium, carbon, and hydrogen analysis confirming to:-



$$x = 0.6 - 0.8$$

$$y = 1.2 - 1.4$$

$$z = 0 - 3$$

6. Calcium/Magnesium - The Ca/Mg mole ratio of water soluble product shall be between 0.25 and 0.67.
7. Insoluble Material - The percent of water insolubles shall be <3%.
8. Product Attrition - The attrition values of CMA shall not exceed those of rock salt as measured by ASTM D 4058-81.
9. Specific Gravity - The specific gravity of CMA shall be >1.2 as measured by ASTM D 70-76 using toluene as the displacement liquid.

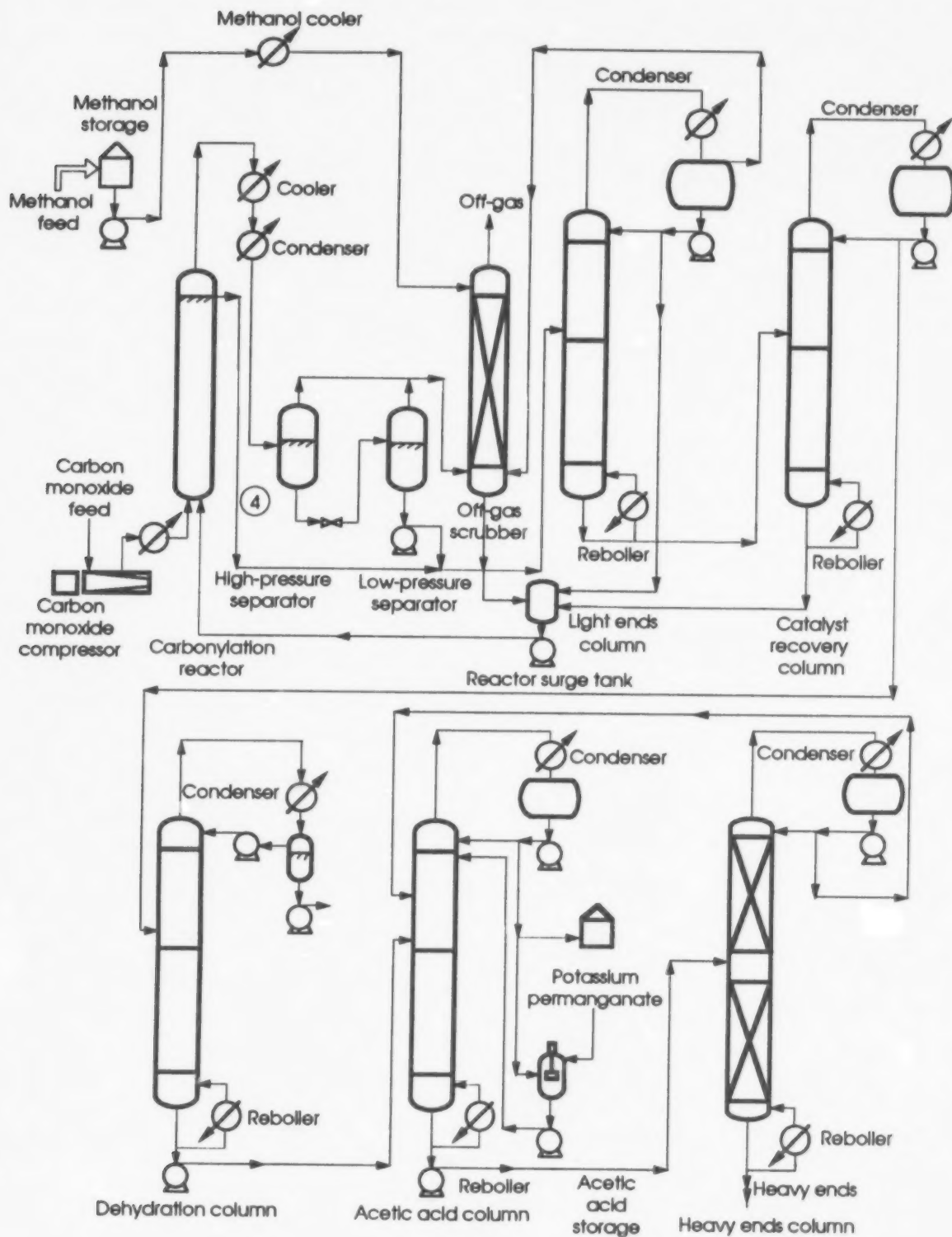


Figure 1/ Acetic acid by carbonylation of methanol typical flow sheet
Adapted from reference 6.

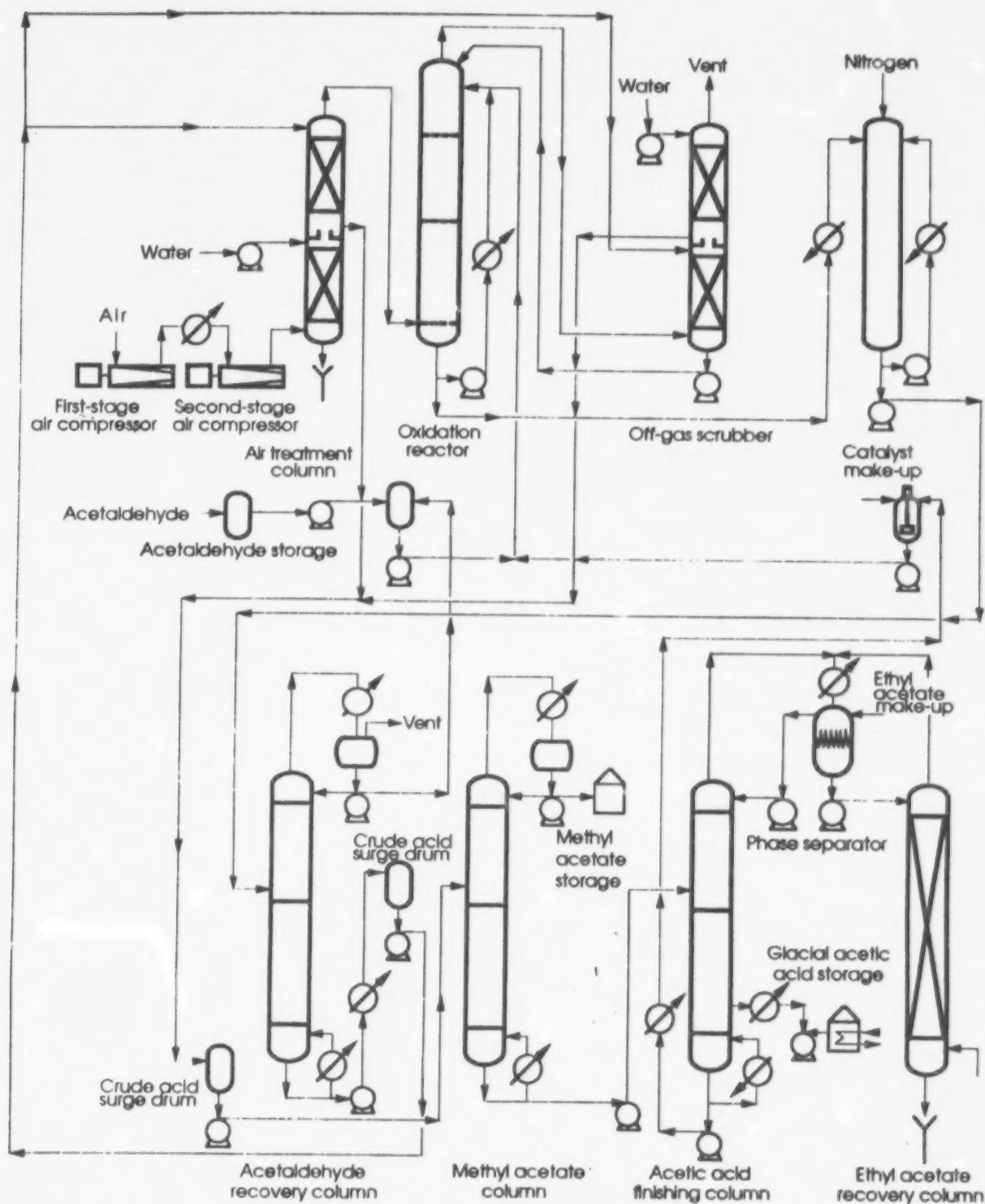


Figure 2/ Acetic acid by acetaldehyde oxidation typical flow sheet
Adapted from reference 6

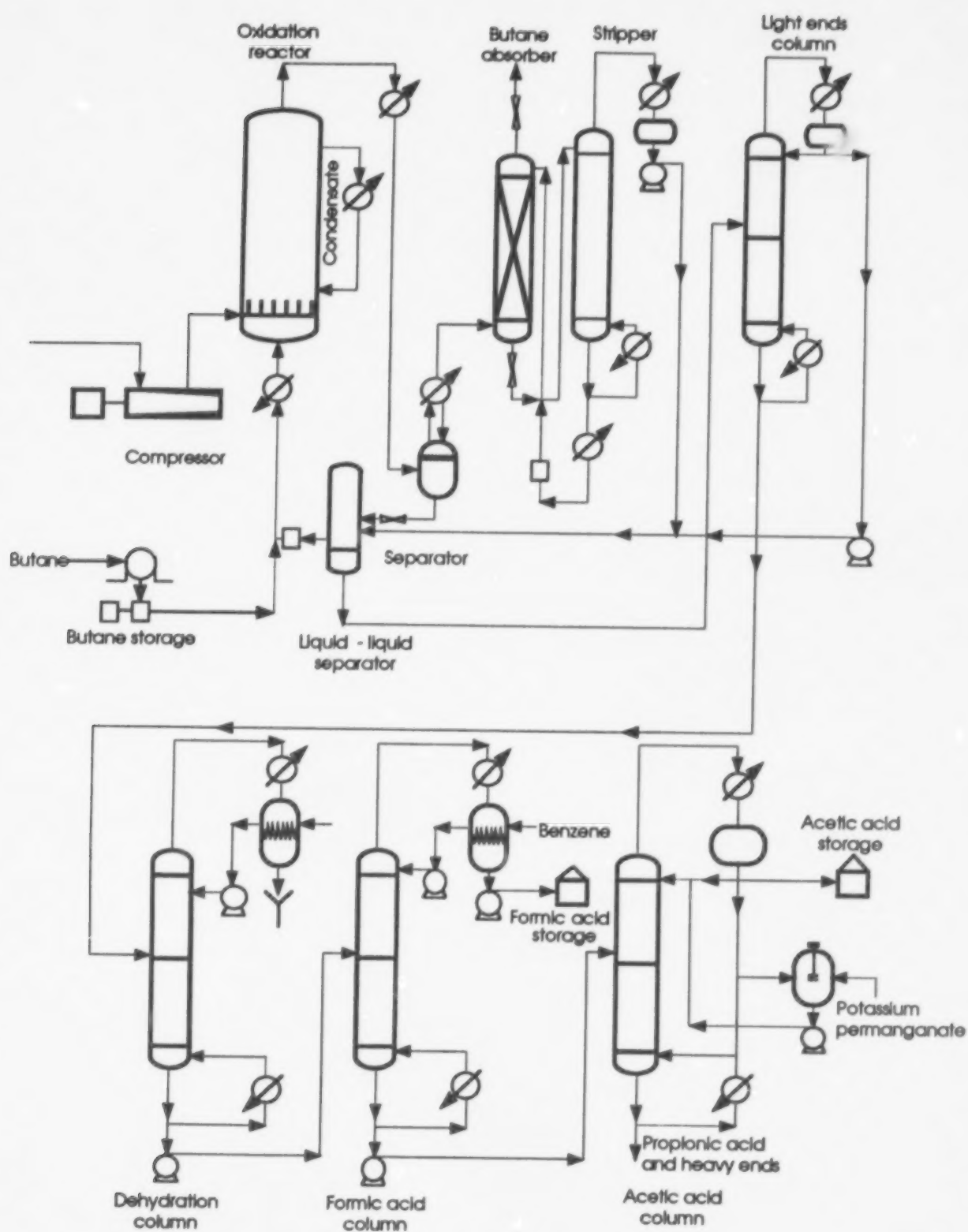


Figure 3/ Acetic Acid by Butane Oxidation typical flow sheet

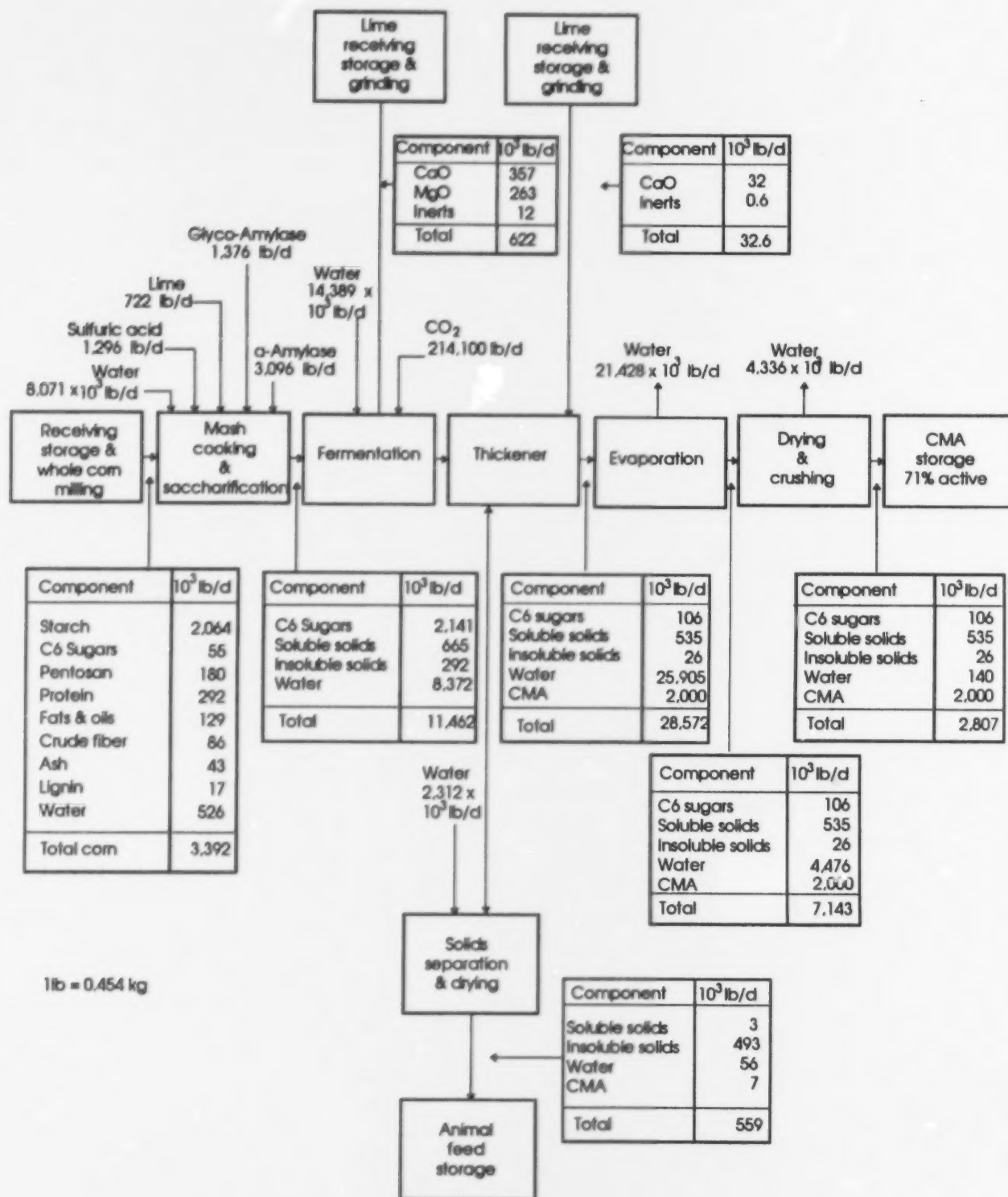


Figure 4/ Block flow diagram for production of CMA from corn grain
Data from reference 16.

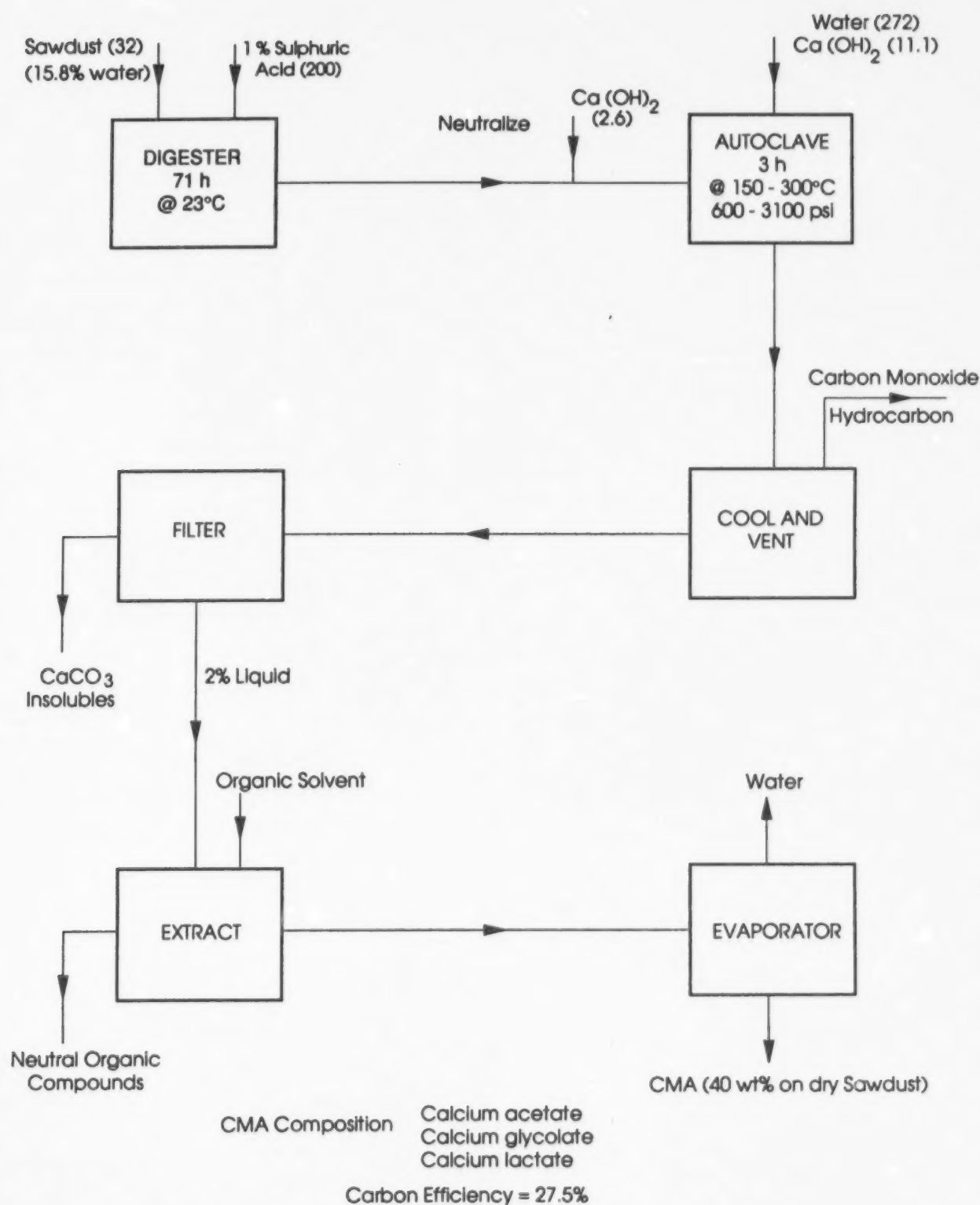


Figure 5/ CMA from cellulosic waste — U.S. patent 4,430,240

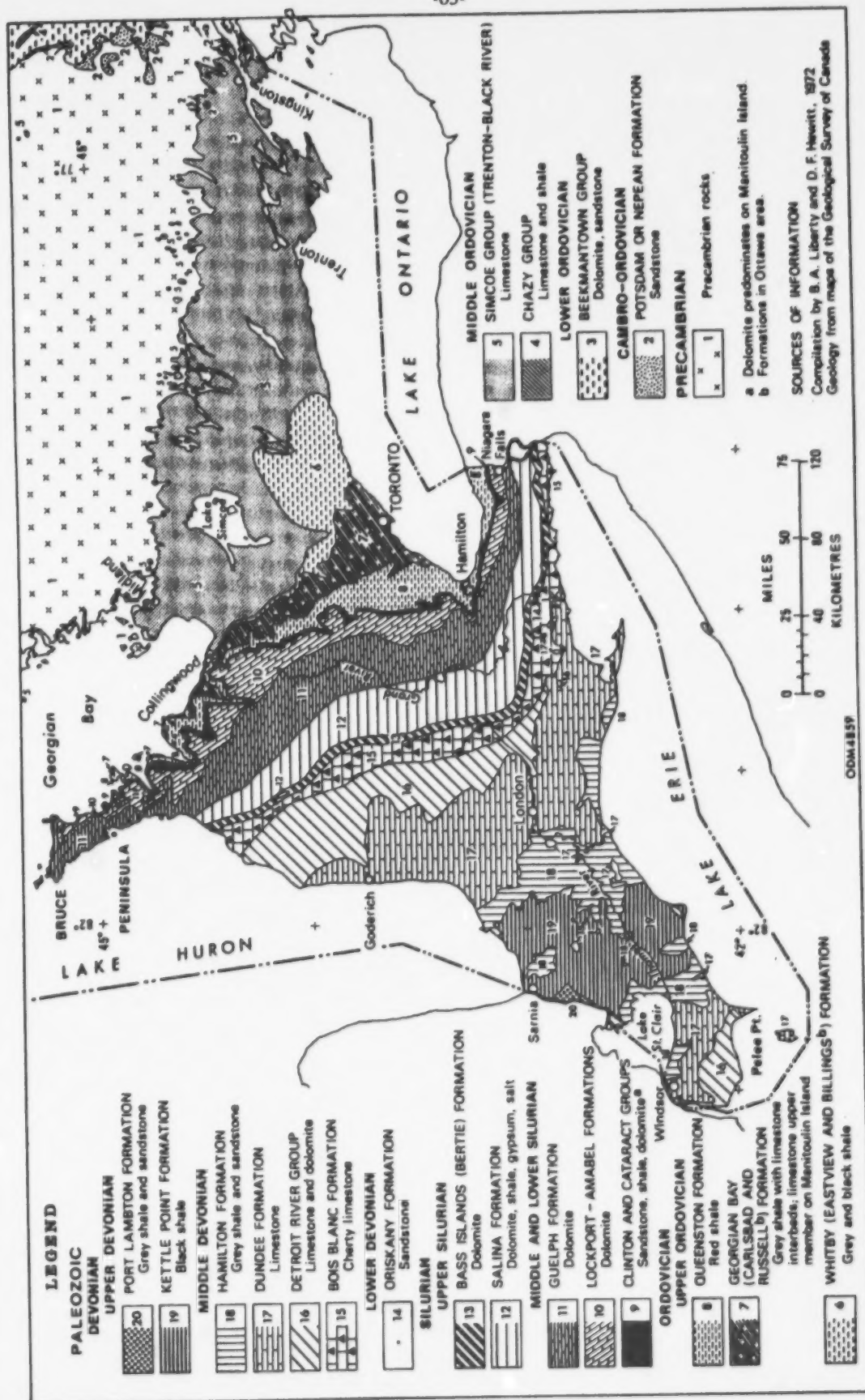


Figure 6 - Regional geology of Great Lakes Lowland in Ontario.

ECONOMIC EVALUATION OF PROCESSES
FOR CMA MANUFACTURE

APPENDIX I

ECONOMIC EVALUATION OF COMMERCIAL PROCESSES FOR CMA
MANUFACTURE USING NATURAL GAS FEEDSTOCK - BASE CASE
STUDY

APPENDIX II

ECONOMIC EVALUATION OF PROCESSES FOR CMA MANUFACTURE
USING ALTERNATIVE FEEDSTOCKS

1. MSW Biomass
2. Wood Biomass

APPENDIX III

ECONOMIC EVALUATION OF A PROCESS FOR CMA MANUFACTURE BY
BACTERIAL FERMENTATION OF CORN DERIVED SUGARS

APPENDIX I

ECONOMIC EVALUATION OF COMMERCIAL PROCESSES FOR CMA MANUFACTURE USING NATURAL GAS FEEDSTOCK

BASE CASE STUDY

ECONOMIC ASSESSMENT OF COMMERCIAL PROCESSES - NATURAL GAS FEEDSTOCK

Scope of Work

The objective was to provide preliminary capital and operating cost estimates for a 1,000,000 t/a CMA plant, including the plant mass and energy balances, based on best currently available technology. This technology was to be commercially proven if possible or otherwise the apparently best available based on published data.

Introduction

The proposed CMA manufacturing complex is based on the following processing units (the Process Flow Diagram is attached):-

- * Natural gas reformer
- * CO separation
- * Methanol synthesis
- * Acetic acid synthesis
- * CO₂ absorption
- * Dolomitic lime manufacture
- * Neutralization, product pelletizing and drying

In view of the very large quantities of natural gas required, i.e. 1.95 Mm³ API/d (69 MM SCFD) vs. about 0.71 Mm³ API/d (25 MM SCFD) for the largest present day Ontario consumer, a processing route incorporating flue gas absorption was selected. Although this approach reduced the original gas consumption estimate by about 0.28 Mm³ API/d (10 MM SCFD), the overall economics of the process remained largely unchanged due to the significant increase in capital cost. However, it was felt that despite the somewhat increased complexity of the plant, the conservation of a finite resource will be regarded as a positive step.

It is possible to reduce natural gas consumption further by substituting another fuel in the kiln operation. Current practice in the cement industry uses coal. The kiln effluent gases using coal would be richer in carbon dioxide and may permit a smaller CO₂ absorption unit to be incorporated. The overall economic effect of this has not been evaluated.

In an alternate processing scheme, the CO₂ absorption system would be replaced with an oxygen plant and CO would be generated by incomplete combustion of natural gas.

SUMMARY

Preliminary capital and operating costs for a 1 M tonne per year CMA plant have been estimated. The most economic processing steps, were selected, an integrated flowsheet developed and mass and energy balances calculated.

The preliminary installed cost, including off-sites and a 35% contingency was estimated at \$726 MM. Additional charges for interest during construction, start-up cost and working capital bring the total capital investment required to about \$880 MM.

The total operating cost, including a 10% contingency, is estimated at \$150/t CMA. Interest on capital investment and depreciation increase the total production cost to approximately \$300/t of CMA produced.

The CMA production cost sensitivity to capital cost, interest rates, labour, natural gas, power and dolostone cost are evaluated. The three factors most affecting CMA price are capital cost, natural gas price and interest rates. A 10% change in capital cost alters the price of CMA by approximately \$10/t.

CMA produced from a 500,000 t/a plant would cost about \$370/t or 22% more than the 1 Mt/a plant.

Major Processing Units

Natural Gas Reforming

The Haldor-Topsoe Sparg process, capable of handling high CO_2/CH_4 ratio was selected. The process uses a sulphur passivated nickel catalyst which prevents carbon nucleation at the high carbon feed content needed to produce the $\text{CO}/\text{H}_2=1$ syngas. The licensor claims lower capital and operating cost than for conventional catalysts. To-date, only one plant uses this technology, but it is a relatively new process. Alternate technology is available from Lurgi.

CO Separation

The Cosorb process, developed by Tenneco Chemicals Inc. and presently marketed by Kinetics Technology International Corp., was chosen. The process utilizes cuprous aluminum tetrachloride in a toluene solvent to selectively absorb CO. The CuAlCl_4 forms a chemical complex with CO. The absorbed gas can be easily stripped at elevated temperature.

The process is claimed to have favorable economics due to the good absorption characteristics of the solvent and the low pressure required, and is relatively free from corrosion and environmental problems. At least two Cosorb plants have been built to-date. Alternate technology: advanced copper zeolite pressure swing absorption (PSA) from Nippon Kokan K.K., which is to be marketed soon and is supposed to be very competitive.

Methanol Synthesis

The Lurgi low pressure methanol process is the leading technology at present. In total 22 plants have been built or are under construction, with nine of them at capacities either equal or exceeding our requirement. Lurgi are claiming high energy recovery ratio (1 to 1.4 kg of steam per kg of methanol) and long catalyst life (4 years). The operating pressure is about 10 MPa in large units, temperature 240 to 270°C, and the catalyst used is probably the usual Cu-Zn formulation. However, Lurgi require a greater degree of commitment on our part before releasing more information on capital requirements and royalty charges. The alternate technology available would be ICI, Huls, etc.

Acetic Acid Synthesis

A superior technology was developed by Monsanto between 1967 and 1970. Now all new acetic acid plants are utilizing this process. Process details were given in Task 1, Process Description.

Monsanto has sold their licensing rights to British Petroleum. BP at present prefer to manufacture the acetic acid by themselves and so exercise control over the marketplace. High level meetings will be required to explain our intentions as to the end use of the acetic acid, to convince them to release at least some basic information regarding the capital cost and royalties. The estimate is based on data available from various literature sources.

Unfortunately, there is no competitive alternate technology available. On the other hand, if further negotiations with BP are unsuccessful, the technology could perhaps be gained from some longtime process users, as the original Monsanto patent protection has either expired or is due to expire soon.

CO₂ Absorption

The absorption of CO₂ from flue gases is rarely economical. However, a new process by Dow Chemical U.S.A.'s Gas Spec. Group and Procon International Inc. (a UOP Inc. subsidiary) is supposed to have an edge over the older ethanolamine (MEA, DEA and MDEA) based technologies.

The Dow-Procon process uses the Dow proprietary alkanolamine based solvent called Gas/Spec FS-1L in combination with an energy saving system developed by Procon. Alternate technology: replace by an oxygen plant and generate CO in a direct route. Our preliminary calculations indicate the costs will be approximately equal for both approaches, however the CO₂ absorption process would save natural gas.

Dolomitic Lime Production

In view of reliability of data on cost and energy consumption, an equipment configuration consisting of a rotary kiln with limestone preheater was selected. However, a more advanced vertical kiln could potentially reduce the natural gas consumption by about \$1.30 per t of CMA, with only a marginally higher capital cost. Of course, additional savings could be realized by operating a dolostone quarry rather than purchasing dolostone.

Neutralization, Pelletizing and Product Drying

The U.S. Department of Transportation, Federal Highway Administration commissioned a pilot plant study, which uses a drum pelletizer to directly react the unslaked dolomitic lime with approximately 80% acetic acid. Since this appears to be the best technology for solid CMA production at present, the data from the above study form the design basis of our final processing step. Details on the alternate technology used by Chevron are not publicly available.

Mass and Energy Balances

The following economic evaluation is based on the mass and energy balances presented in the Appendix.

Preliminary Capital Cost Estimate

The capital cost estimate is based on direct licensor information, where available; otherwise published data were scaled proportionately and escalated to mid-1988 \$ Canadian.

The plant was assumed to be located in southern Ontario. There are essentially two possibilities here: (i) locate the plant near a dolostone deposit and ship the product CMA, or (ii) locate the plant near a Great Lakes harbour and ship either dolostone (0.58 t/t CMA) or dolomitic lime (0.3 t/t CMA) to the plant. The second option would probably lower the overall shipping expense, as cheaper water transport could be utilized for CMA distribution to several strategically located depots.

To minimize the capital cost, the plant is designed on a single train basis where practical, but two or more trains had to be considered for certain processing units.

Unfortunately, very little information was published on acetic acid plant costs. As mentioned before, the licensor refused to release any information on a preliminary basis. Data for similar, older technologies had to be utilized to approximate the Monsanto process capital cost. Fortunately, the new technology is claimed to have lower capital and operating costs.

The overall capital cost is estimated to be about +25% accurate. A summary table of the preliminary capital cost is presented in the Appendix. The preliminary installed cost, including off-sites and 35% contingency is estimated at \$726 MM. When interest during construction, start-up cost and working capital are added, the total capital investment required will be about \$880 MM.

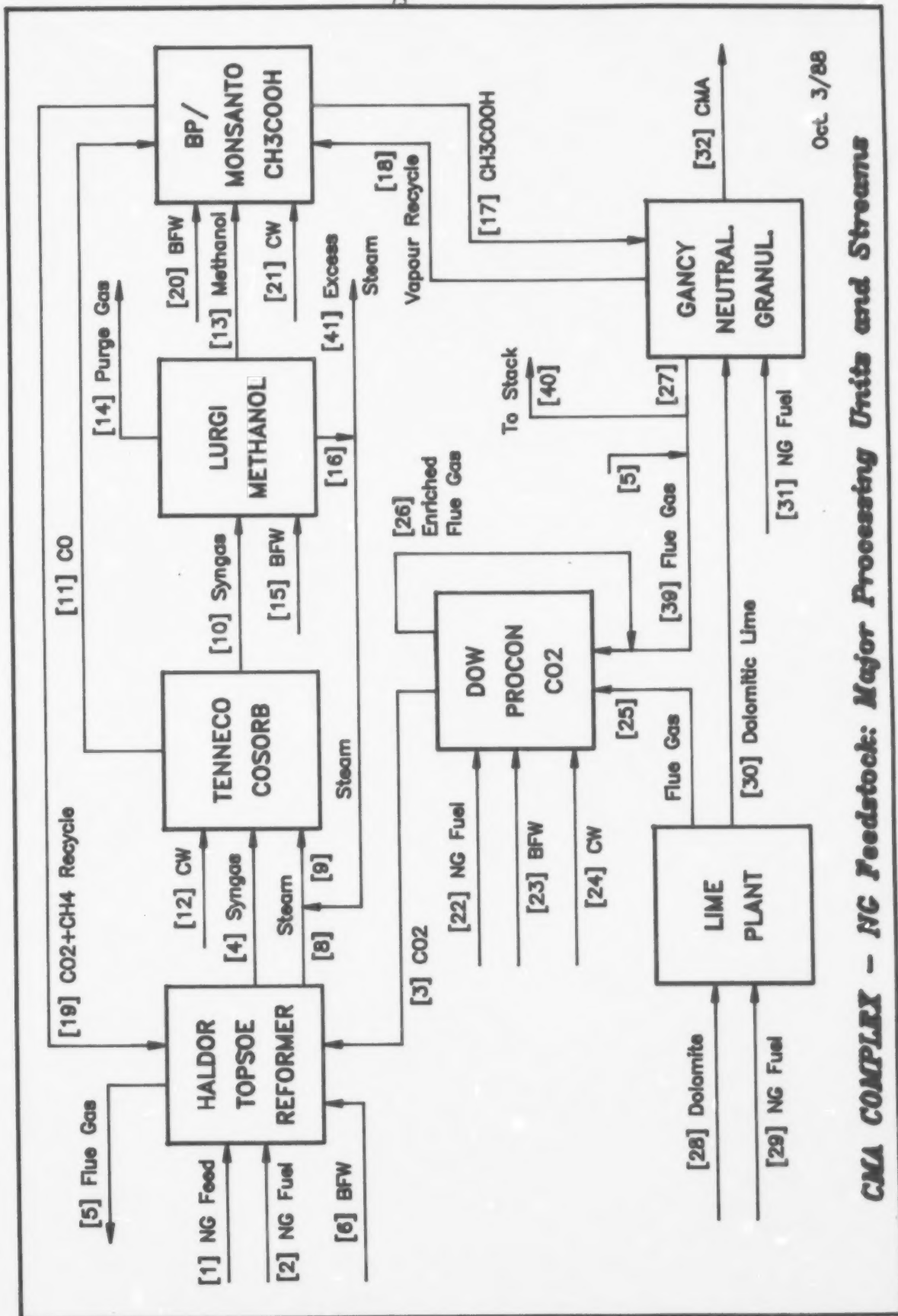
Operating Cost

In the operating cost estimate, 100% utility type financing at 11% interest rate was assumed. The interest rate affects the total production cost of CMA, i.e. for every one percent change in the interest rate, the CMA price will change by \$9/t. The uncertainty in the capital cost affects the production cost as follows: for every \$ 100 MM (11%) difference in the capital cost, the production cost will change by about \$25/t of CMA (8%). The plant depreciation was taken at 7.5%.

Details of the operating cost estimate are summarized in the attached table. The total operating cost, including 10% contingency, was estimated at about \$150/t CMA, and when interest on capital investment and depreciation are included, the overall production cost of CMA is calculated to be about \$300/t.

APPENDIX

1. CMA Manufacturing Complex - Natural Gas Feedstocks
2. Flow Diagram - CMA Manufacturing Complex
3. Mass and Energy Balances
4. Preliminary Capital Cost Summary Table
5. Preliminary Operating Cost Summary Table



Oct. 3/88

CMA COMPLEX - NG Feedstock: Major Processing Units and Streams

MASS BALANCE - 1 MM m^3/yr CMA PLANT - NG Feedstock

Page 1

Stream	1	2	3	4	5	6	8	9	10	11	12	13	14	15	16
Flowrate (m^3/hr)	NG Feed	NG Fuel	CO_2 Syngas(1/1)	Flue Gas	BFM	Steam	Steam	Steam	Syngas(1/2)	CO	CM	Methanol	Purge Gas	BFM	LP Steam
H_2				6.72					6.72				0.33		
N_2	0.75												0.75		
CH_4	23.23	15.80													
C_2H_6	0.40														
CO				93.37					46.69	46.69			2.27		
CO_2	0.33		82.63												
H_2O											2118.68			61.57	20.52
O_2								70.64				51.30			
CH_3OH															
CH_3COOH															
$0.5\text{CaHg}(\text{CO}_3)_2$															
0.5CaHgO_2															
CMA															
CMA, 1/2 H_2O															
Totals															
kgmole/hr	1560.36	984.88	1877.54	6667.12					5000.34	1666.78		1601.13	269.83		
m^3/hr	24.71	15.80	82.63	100.10					53.41	46.69	2118.68	51.30	3.35	61.57	20.52
m^3/hr	34951.97	22061.28	42056.98	149343.47					112007.60	37335.87	2118.68		6044.22	61.57	20.52
MSCF/hr	1234.18	779.00	1485.23	5274.01					3955.51	1318.50			213.45		

September 15, 1968

MASS BALANCE - 1 NH 07/yr CMA PLANT - NS Feedstock

Stream	31	32	34	35	36	37	38	39	40	41
Flowrate (mT/hr)	N6 Fuel	CMA	Total Fuel	Total N6	Total Flue Gas	Total BFW	Total CW	D-P Feed	Excess Flue Gas	Excess Steam
H2										
N2										
CH4	5.63		34.87	58.10						
C2H6										
CO										
CO2										
H2O					130.53	165.04	12274.57	61.21	69.32	13.43
O2										13.43
CH3OH										
CH3COOH										
0.5CaMg(CO3)2										
0.5CaMgO2										
CMA		119.12								
CMA. 1/2 H2O		126.26								
Totals	351.19	792.64	2173.29	3621.30	130.53	165.04	12274.57	61.21	69.32	13.43
kgmole/hr										
mT/hr	5.63	126.26	34.87	58.10						
m3/hr	7866.67	48681.62	48681.62	81117.05						
MSCF/hr	277.78	1719.18	1719.18	2864.62						

PRELIMINARY CAPITAL COST ESTIMATE
1MM mT/yr CMA Plant - NG Feed

Oct. 3/88

Unit	\$ MM
1. Haldor-Topsoe Sparg Shift	80
Off-sites	35
2. Tenneco Cosorb CO Absorption	25
Off-sites	12
3. Lurgi Methanol Synthesis	82
Off-sites	28
4. BP-Monsanto Acetic Acid Synthesis	100
Off-sites	20
5. DOW-Procon CO2 Absorption	63
Off-sites	30
6. Dolomitic Lime Manufacture	30
Off-sites (Included above)	0
7. Gancy CMA Neutralization, Granulation and Drying	33
Off-sites (Included above)	0
SUB-TOTAL	538
Contingency (35 %)	188
TOTAL FIXED INVESTMENT	726
Interest During Construction (15 %)	109
Start-up Costs (2 %)	15
Working Capital (30 d inventory)	30
TOTAL CAPITAL INVESTMENT	880

PRELIMINARY OPERATING COST ESTIMATE

1 MM mT/yr CMA Plant - NG Feed

Oct. 3/88

FEEDSTOCKS AND UTILITIES

	Units	Cons./hr	\$/unit	\$/yr	\$/mT CMA
Natural Gas	MSCF	2865	2.55	\$57,861,540	\$57.86
Dolomite	mT	73.1	7	\$4,052,664	\$4.05
Power	kWh	41600	0.0375	\$12,355,200	\$12.36
Steam (included in fuel)					
Cooling Water	m3	2455	0.0375	\$729,135	\$0.73
Boiler Feedwater	m3	165	0.25	\$326,700	\$0.33

SUB-TOTAL

\$75,325,239 \$75.33

CATALYSTS AND CHEMICALS

Reforming (Unit #1)				\$312,500	\$0.31
Toluene (Unit #2)	kg	3.92	0.3	\$9,314	\$0.01
Methanol (Unit #3)				\$254,000	\$0.25
Acetic Acid (Unit #4) Est.				\$500,000	\$0.50
CO2 Absorption (Unit #5)				\$1,721,000	\$1.72

SUB-TOTAL

\$2,796,814 \$2.80

LABOUR

	Manpower	\$/man.yr	\$/yr	\$/mT CMA
Operating Labour (OL)				
Shift Foreman	30	\$35,000	\$1,050,000	\$1.05
Shift Operator	63	\$30,000	\$1,890,000	\$1.89
Day Operator	12	\$25,000	\$300,000	\$0.30

SUB-TOTAL (OL)

\$3,240,000 \$3.24

Supervision (OLS) (15 % OL)			\$486,000	\$0.49
Maintenance L. & Supervision (ML+MLS) (100%(OL+OLS))			\$3,726,000	\$3.73
Administration & Support L. (20 % (OL+OLS+ML+MLS))			\$1,490,400	\$1.49
Payroll Benefits (25 % of all labour cost)			\$2,235,600	\$2.24

TOTAL LABOUR COST

\$11,178,000 \$11.18

Maintenance Materials (2.25 % FI)			\$16,335,000	\$16.34
Insurance & Local Taxes (2 % FI)			\$14,520,000	\$14.52
General Overhead (2 % FI)			\$14,520,000	\$14.52
Royalties (Estimated)			\$3,000,000	\$3.00

SUB-TOTAL

\$137,675,053 \$137.68

Contingency (10 %)			\$13,767,505	\$13.77
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TOTAL OPERATING COST

\$151,442,558 \$151.44

Interest (11 % TCI)			\$96,800,000	\$96.80
Depreciation (7.5 % FI)			\$54,450,000	\$54.45

TOTAL PRODUCTION COST

\$302,692,558 \$302.69

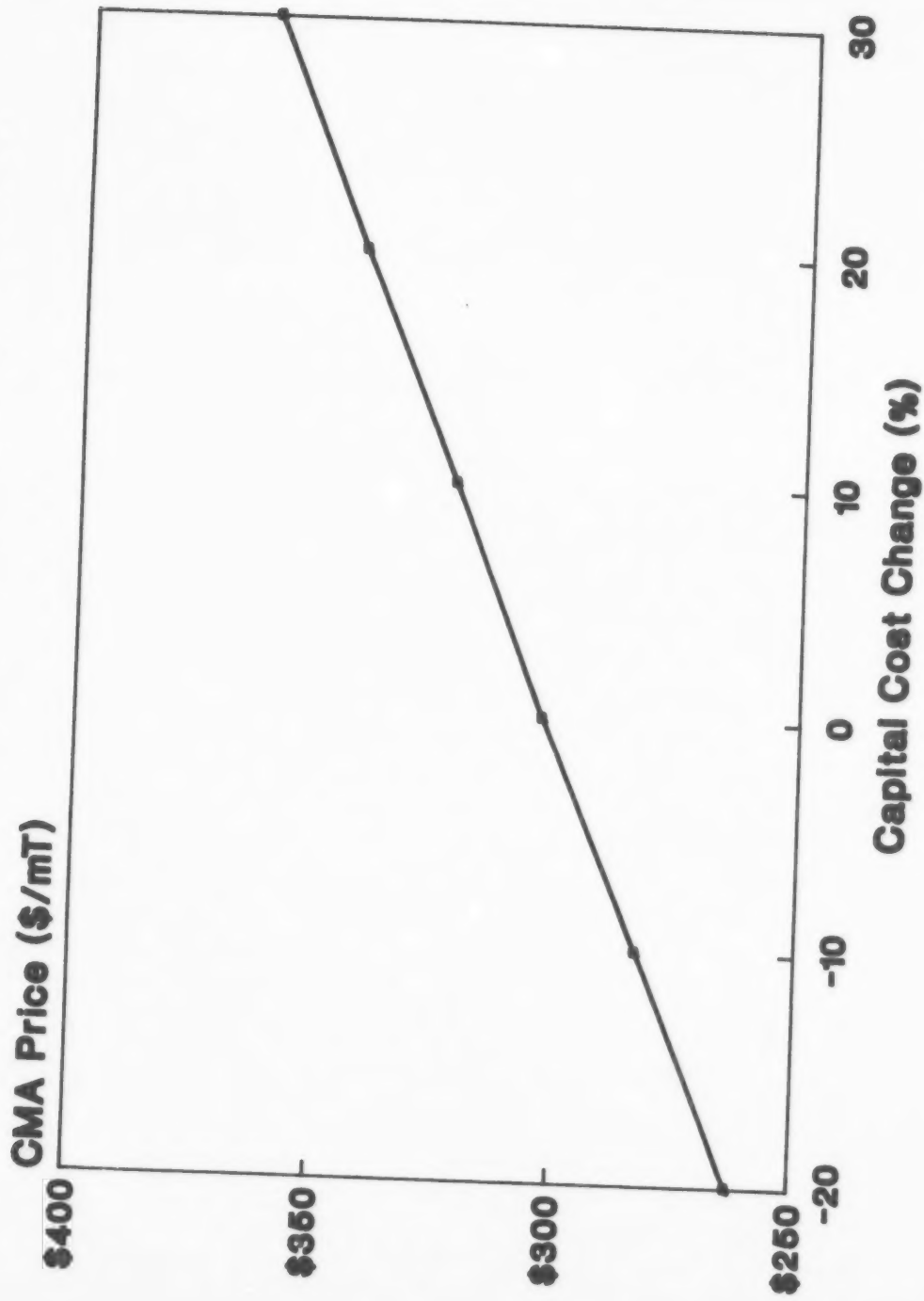
SENSITIVITY

The CMA price sensitivity to capital cost, interest rates, labour, natural gas, power and dolomite cost was evaluated for the Base Case - 1 Mt/a CMA plant with natural gas feedstock.

As expected, the CMA price is most sensitive to changes in capital cost, followed by changes in the natural gas price and interest rates. However, fluctuations in the labour, power and dolomite cost have only a minor influence on the price of CMA.

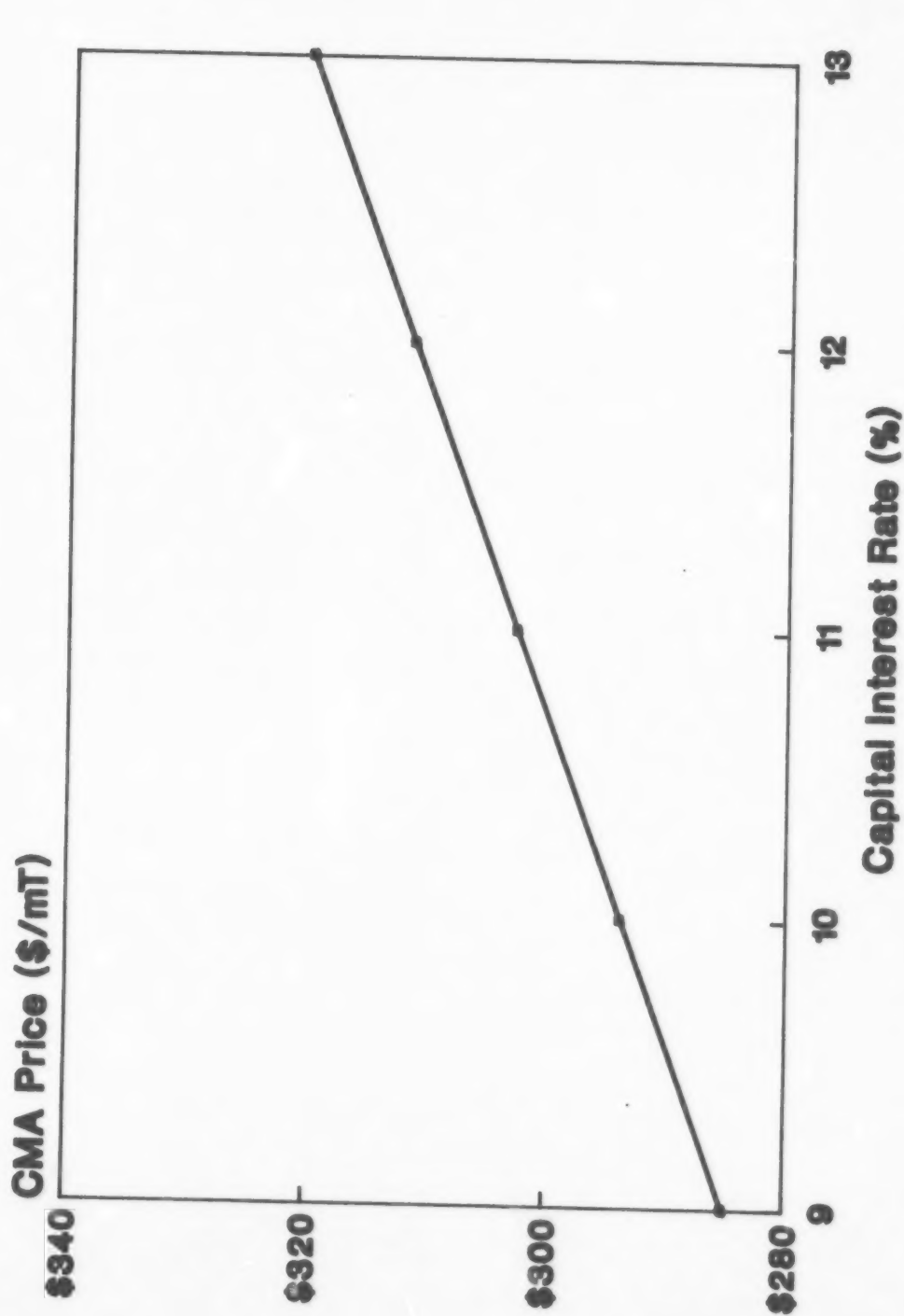
The results of detailed calculations are summarized in the following diagrams.

CMA Price Sensitivity to Capital Cost



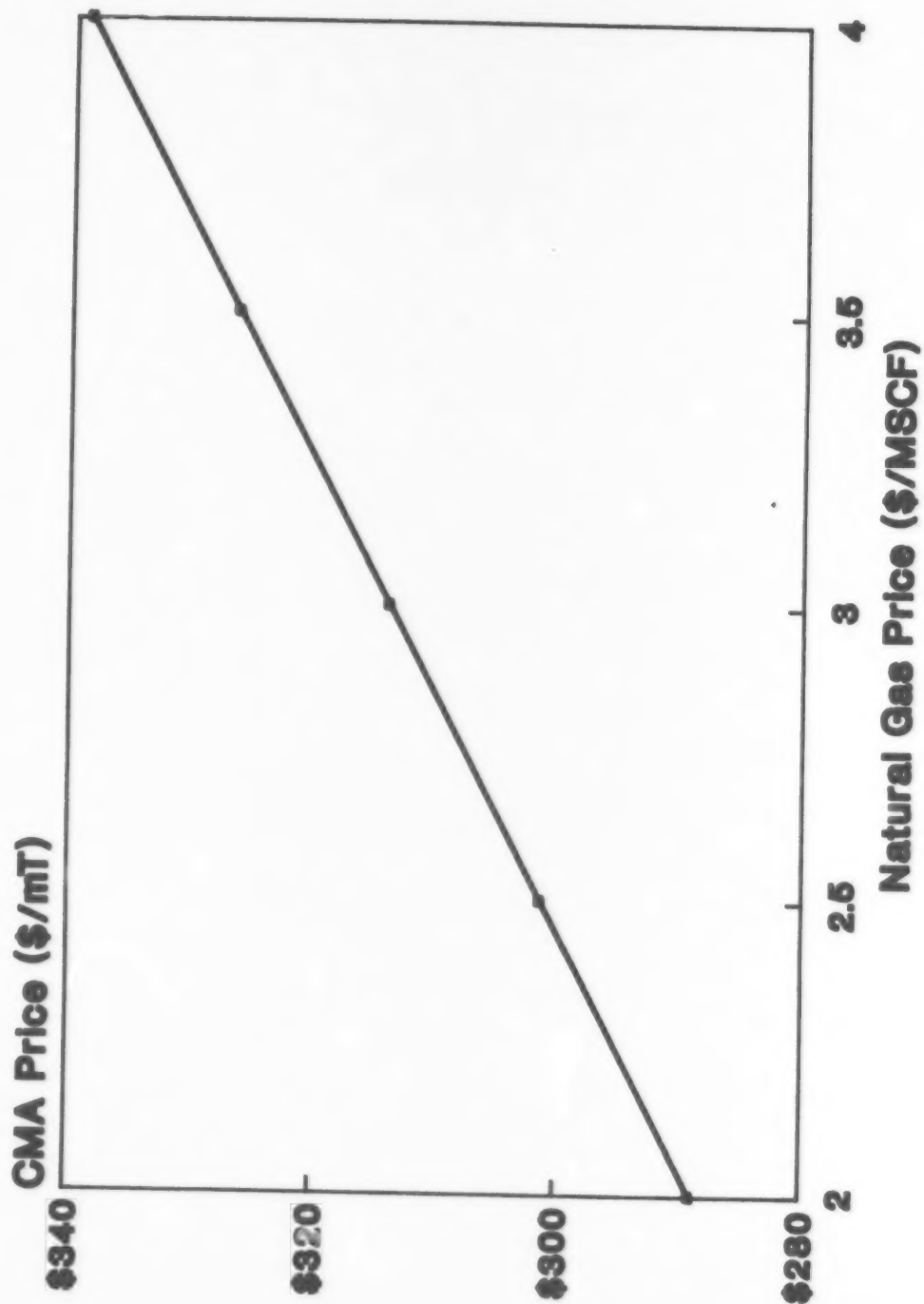
Mid 1988 \$ Can. Basis

CMA Price Sensitivity to Interest Rates



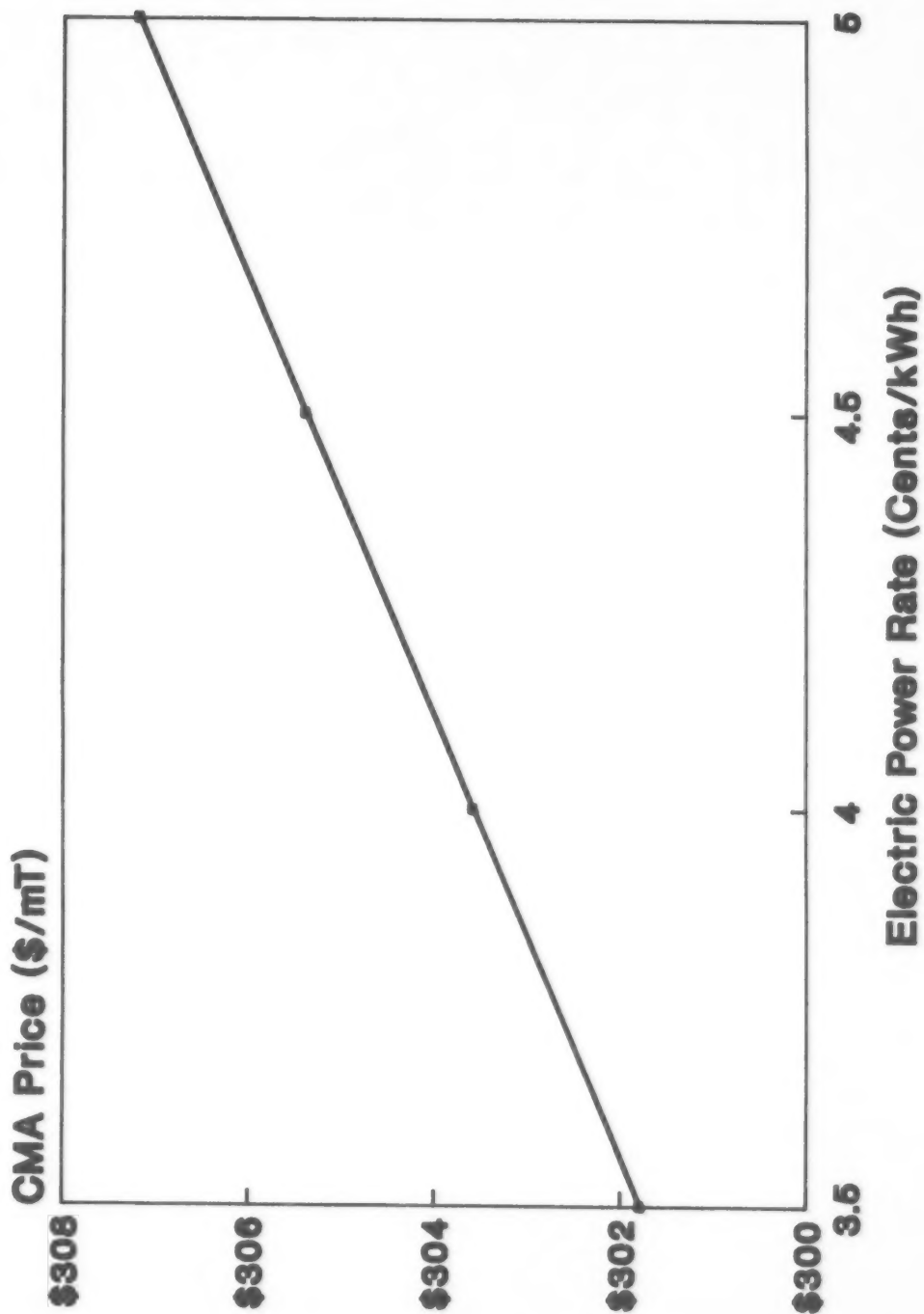
Mid 1988 \$ Can. Base

CMA Price Sensitivity to NG Price



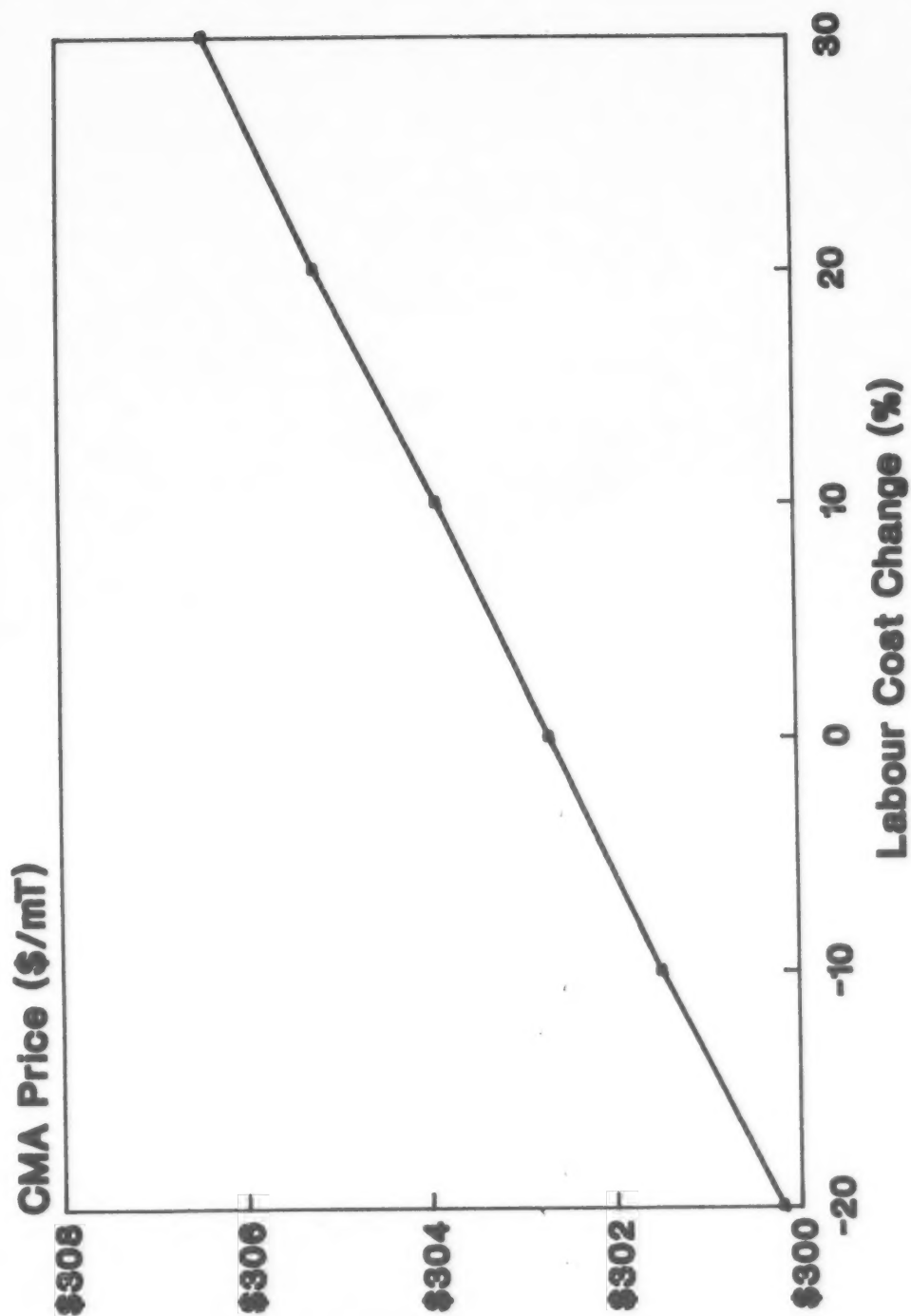
Mid 1988 \$ Can. Basis

CMA Price Sensitivity to Power Rates



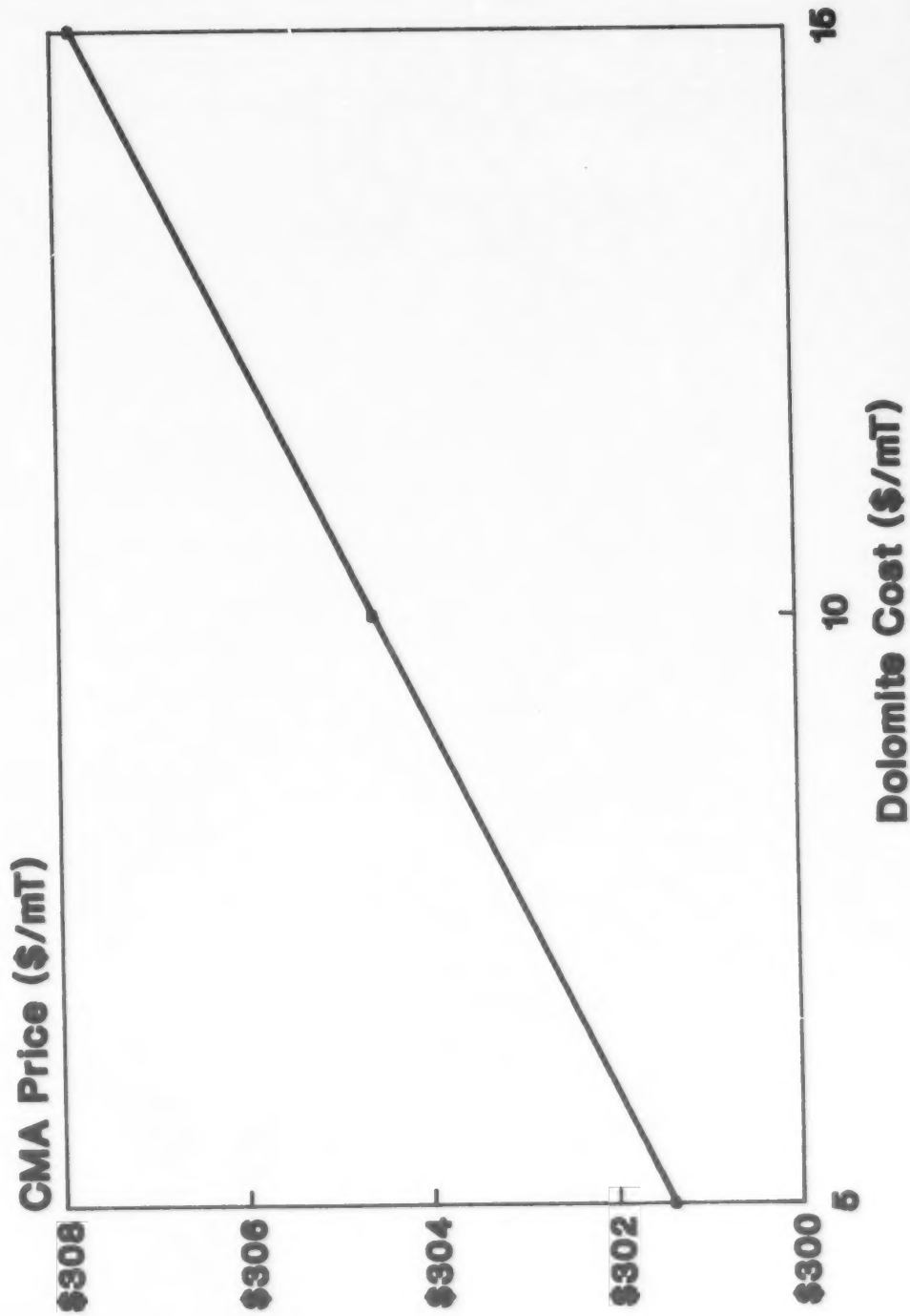
Mid 1988 \$ Can. Base

CMA Price Sensitivity to Labour Cost



Mid 1988 @ Can. Base

CMA Price Sensitivity to Dolomite Cost



Mid 1988 \$ Can. Base

TWO 500 000 Mt/a PLANTS SCENARIO

The capital and operating cost were evaluated for two 500 000 t/a plants. The total capital investment required is estimated at \$1,100 MM, or about 25% higher than for a single plant.

The total operating cost, including amortization and interest on capital charges, was estimated at \$369 per t of CMA, or about 22% higher than for a single 1 MM t/a plant.

Details of the capital and operating cost estimates are presented in the following tables.

PRELIMINARY CAPITAL COST ESTIMATE
0.5 MM mT/yr CMA Plant - NG Feed

May 20/89

Unit	\$ MM

1. Haldor-Topsoe Sparg Shift	50
Off-sites	22
2. Tenneco Cosorb CO Absorption	15
Off-sites	8
3. Lurgi Methanol Synthesis	55
Off-sites	18
4. BP-Monsanto Acetic Acid Synthesis	62
Off-sites	13
5. DOW-Procon CO2 Absorption	40
Off-sites	18
6. Dolomitic Lime Manufacture	20
Off-sites (Included above)	0
7. Gancy CMA Neutralization, Granulation and Drying	18
Off-sites (Included above)	0

SUB-TOTAL	339
Contingency (35 %)	119

TOTAL FIXED INVESTMENT	458
Interest During Construction (15 %)	69
Start-up Costs (2 %)	9
Working Capital (30 d inventory)	15

TOTAL CAPITAL INVESTMENT	550

Mid 1988 \$ Can. Basis

PRELIMINARY OPERATING COST ESTIMATE
0.5 MM mT/yr CMA Plant - NG Feed

May 23/89

FEEDSTOCKS AND UTILITIES

	Units	Cons./hr	\$/unit	\$/yr	\$/mT CMA
Natural Gas	MSCF	1432.5	2.55	\$28,930,770	\$57.86
Dolomite	mT	36.55	7	\$2,026,332	\$4.05
Power	kWh	20800	0.0375	\$6,177,600	\$12.36
Steam (included in fuel)					
Cooling Water	m3	1227.5	0.0375	\$364,568	\$0.73
Boiler Feedwater	m3	82.5	0.25	\$163,350	\$0.33

SUB-TOTAL

CATALYSTS AND CHEMICALS

\$37,662,619 \$75.33

Reforming (Unit #1)				\$312,500	\$0.31
Toluene (Unit #2)	kg	1.96	0.3	\$4,657	\$0.01
Methanol (Unit #3)				\$254,000	\$0.25
Acetic Acid (Unit #4) Est.				\$500,000	\$0.50
CO2 Absorption (Unit #5)				\$1,721,000	\$1.72

SUB-TOTAL

\$2,792,157 \$2.80

LABOUR

	Manpower	\$/man.yr	\$/yr	\$/mT CMA
Operating Labour (OL)				
Shift Foreman	30	\$35,000	\$1,050,000	\$2.10
Shift Operator	60	\$30,000	\$1,800,000	\$3.60
Day Operator	8	\$25,000	\$200,000	\$0.40

SUB-TOTAL (OL)

\$3,050,000 \$6.10

Supervision (OLS) (15 % OL)			\$457,500	\$0.92
Maintenance L. & Supervision (ML+MLS) (100%(OL+OLS))			\$3,507,500	\$7.02
Administration & Support L. (20 % (OL+OLS+ML+MLS))			\$1,403,000	\$2.81
Payroll Benefits (25 % of all labour cost)			\$2,104,500	\$4.21

TOTAL LABOUR COST

\$10,522,500 \$21.05

Maintenance Materials (2.25 % FI)			\$10,305,000	\$20.61
Insurance & Local Taxes (2 % FI)			\$9,160,000	\$18.32
General Overhead (2 % FI)			\$9,160,000	\$18.32
Royalties (Estimated)			\$2,000,000	\$4.00

SUB-TOTAL

\$81,602,276 \$163.20

Contingency (10 %)			\$8,160,228	\$16.32
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TOTAL OPERATING COST

\$89,762,504 \$179.53

Interest (11 % TCI)			\$60,500,000	\$121.00
Depreciation (7.5 % FI)			\$34,350,000	\$68.70

TOTAL PRODUCTION COST

\$184,612,504 \$369.23

Mid 1988 \$ Can. Basis

APPENDIX II

ECONOMIC EVALUATION OF PROCESSES FOR CMA MANUFACTURE USING ALTERNATIVE FEEDSTOCKS

- 1) MSW BIOMASS
- 2) WOOD BIOMASS

Summary

Preliminary capital and operating cost for a 1 M tonnes per year CMA plant have been estimated for two alternative processing schemes using the same basic assumptions used in the base case. For each case attempts were made to select the most economic processing steps then develop an integrated flow sheet and calculate mass and energy balances.

The following represent the preliminary installed cost estimates, including off-sites and a 35% contingency for each of the two cases and data generated on the SRI route based on corn fermentation (Appendix III).

	<u>Installed Cost \$MM</u>	<u>Total Capital \$MM</u>	<u>Operating Cost \$/t CMA</u>	<u>Net Production Cost \$/t CMA</u>
MSW Biomass	1019	1223	145	341
Wood Biomass	937	1126	233	428
Corn Fermentation	703	853	421	530

Total capital required includes interest during construction, start up costs and working capital.

ECONOMIC ASSESSMENT OF BIOMASS SOURCES FOR CMA MANUFACTURE

Introduction

One of the largest single sources of low cost biomass is municipal solid waste (MSW). The traditional disposal routes of MSW, landfill or direct incineration are becoming increasingly unacceptable due to environmental concerns.

Utilizing the MSW biomass for CMA manufacture would therefore represent a very attractive manufacturing route from the environmental, and the energy conservation aspect.

Wood as the forest industry waste is another potentially large source of biomass. For utilization of wood two basic processing routes are available: (1) thermochemical processes, such as gasification and pyrolysis, and (2) wet chemical and biochemical processes, such as hydrolysis followed by microbiological fermentation.

However, wood waste based biomass is a more diffuse feedstock source than MSW, and higher handling and collection costs are to be expected.

The agricultural products and waste materials represent another potential feedstock source for CMA manufacture. Of these, corn is the most suitable and readily available source of starch for microbiological conversion.

MSW BIOMASS SOURCE

MSW Availability

Studies conducted in the Peel and Halton regions indicated that about 0.727 t of suitable MSW is generated per capita annually. This quantity includes most of the residential waste available, and about one half of the commercial/industrial waste generated. The remaining half of the latter is essentially non-combustible.

With the above figure, and assuming that there are about three million inhabitants in the metropolitan Toronto area, we get potentially about 6600 t per day of raw MSW.

At present, there are two MSW projects under study in the Halton/Peel regions. The Petro-Sun SNC-EFW project is planned to incinerate MSW to generate electricity and the St. Lawrence Cement Refuse Derived Fuel (SLC-RFD) project is being designed to supply MSW based fuel as a partial replacement of coal for firing cement kilns. Because the SLC-RFD project has to supply relatively low ash fuel, large proportions of the available biomass are rejected in the sorting process (69%). The Petro-Sun project, however, postulates the following MSW breakdown:

Materials recovered.....	12 %
Incinerated.....	58 %
Landfill.....	30 %.

For our study, we have adopted the Petro-Sun figures, although using a slagging gasifier is expected to yield somewhat less slag than the ash obtained by air incineration of MSW.

Based on the above MSW breakdown and published cost for MSW shredding and sorting of \$17 per t (amortized cost), the CMA complex will require a tipping fee of about \$30 per t, to obtain biomass feedstock at zero price. There will be a potential credit for materials recovered from the raw MSW, such as steel, aluminum and glass. The shipping costs for these materials are assumed to be offset by savings on the discharge tipping fees.

After shredding and sorting, the postulated MSW quantity drops to about 5800 t per day. Based on optimum synthesis gas composition, with some natural gas used to supplement the hydrogen poor MSW derived gas, around 5550 t per day of sorted MSW could be utilized as CMA plant feedstock. This estimate is a very flexible one, as more MSW, if available, could be utilized to replace some of the natural gas fuel still required; or vice versa, almost any quantity of MSW could be replaced by natural gas. Actually, the hybrid "MSW - natural gas" feedstock based plant would have the advantage in approaching an optimum synthesis gas composition directly without any additional equipment requirement. Nevertheless, the presented design case should provide the basic economic data for assessment of the use of MSW feedstock.

Major Processing Equipment

Purox Unit

The Purox process is a high temperature partial oxidation of solid waste to produce a medium energy or synthesis gas. The MSW is charged at the top of a shaft furnace. The MSW is pyrolyzed as it passes downward through the furnace. Oxygen enters the furnace through tuyeres near the furnace bottom and moves upward through a 1425 to 1650°C combustion zone. The products of combustion pass through a pyrolysis zone and exit at about 90°C. The off-gas then enters an electrostatic precipitator to remove the solid particles and pyrolysis oil droplets, both of which are recycled to the combustion zone. The gas is then treated in an acid absorber and cooled in a condenser.

The Purox system requires a 1250 t per day oxygen plant, which also supplies oxygen to the autothermal reformer. About 1500 m³ per day of waste water will be generated. This water will be treated in a biological waste water treatment unit operating at 99+% efficiency.

A 200 short ton per day facility was built in South Charleston, West Virginia, after a pilot facility has been successfully operated in Tonawanda, New York. Several larger units have been built in Japan.

Alternative gasifier designs are available e.g. Winkler.

Reformers

In addition to a conventional natural gas reformer producing the highest possible ratio of H_2/CO synthesis gas, a catalytic autothermal reformer is needed to reform methane and ethane produced in the Purox process to synthesis gas. The Lurgi reformer could be used here. This reformer is strategically located at the methanol plant purge gas loop, as this gives the lowest possible volume of gas to be treated.

For the conventional natural gas reformer, a conventional Haldor Topsoe unit was employed, but any standard process could be used.

CO₂ Absorption

For this duty, the Selexol process was chosen. However, a number of other processes could be utilized as well.

The remaining equipment remains essentially identical to the equipment described in the natural gas based CMA plant (Appendix I).

Preliminary Capital Cost Estimate

The MSW biomass based CMA complex capital cost are estimated at \$1019 MM. The interest during construction, start-up costs and the working capital required will increase this to about \$1223 MM. These figures have been derived using assumptions and limitations described in the capital cost section for the natural gas based plant.

Operating Cost

For 100% utility type financing at 11%, the CMA price will be about \$340 per t, i.e. about 10% more than for CMA produced from natural gas only. The cost of CMA from a "hybrid feed" natural gas - MSW plant can be interpolated from the two figures.

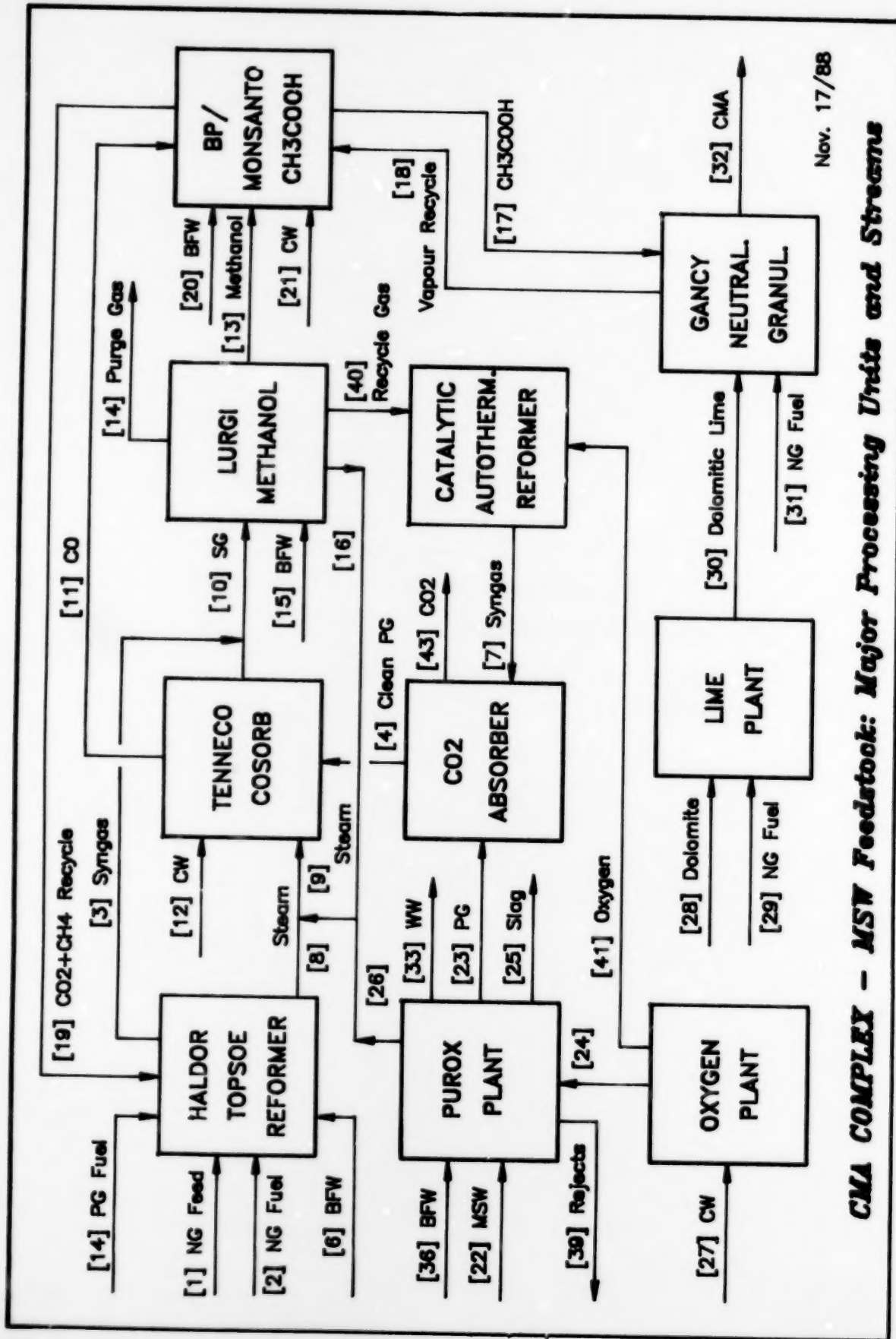
Tipping fees in excess of \$30/t would further reduce the cost of CMA. A tipping fee of \$50/t would give CMA at essentially the \$300/t calculated for the natural gas base case.

WOOD BIOMASS SOURCE

A preliminary operating cost estimate was prepared using the assumption that equipment essentially identical to that used in the MSW gasification will be required. This is, of course, without the MSW shredding and sorting facilities. Shredded forest biomass at \$60 per tonne equates to a CMA production cost of approximately \$425 per tonne.

CMA Manufacturing Complex - MSW Feedstock

- 1) Flow Diagram
- 2) Mass and Energy Balances
- 3) Preliminary Capital Cost Summary Table
- 4) Preliminary Operating Cost Summary Table



Nov. 17/88

CMA COMPLEX - MSW Feedstock: Major Processing Units and Streams

Page 1

MASS BALANCE - 1 MM MT/yr CMA PLANT - NSM Feedstock

Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Flowrate (MT/hr)	NG Feed	NG Fuel Syngas	(1/3) Clean P6 Syngas	(1/1) BFW	Syngas	Steam	Steam	Steam	Syngas(1/2)	CO	CM	Methanol	Purge Gas	BFW LP Steam		
H2			1.97	5.06	7.03	1.20			7.03				0.72			
N2	0.27		0.27	1.67	1.95				1.95				1.67			
CH4	5.23	0.79		3.35	3.35				3.35				0.00			
C2H6	0.16			1.80	1.80				1.80				0.00			
CO			9.14	89.25	98.39	9.22			51.70	46.69			5.01			
CO2	0.12			0.76	0.76				0.76				0.88			
H2O					23.14	17.26	70.64				2118.68			61.57	20.52	
O2												51.30				
CH3OH																
CH3COOH																
0.5C6H6(CO3)2																
0.5C6H6O2																
CMA																
CMA 1/2 H2O																
Totals																
kgole/hr	343.94	49.03	1314.73	6041.48	7356.21	924.42			5689.43	1666.78		1601.13	614.63			
MT/hr	5.78	0.79	11.39	101.89	113.27	10.42	17.26	70.64	66.58	46.69	2118.68	51.30	8.28	61.57	20.52	
M3/hr	7704.27	1098.27	29449.66	135329.22	164764.28	23.14	20706.95	17.26	127443.21	37335.87	2118.68		13767.78	61.57	20.52	
MSCF/hr	272.04	38.78	1040.02	4778.57	5818.60	731.27			4500.61	1318.50			486.20			

November 15, 1968

MASS BALANCE - 1 MM MT/yr CMA PLANT - MSW Feedstock

Page 2

Stream	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Flowrate (MT/hr)	CH ₃ COOH	HAC+H ₂ O Rec.	CO ₂ +CH ₄ Rec.	BFM	CW	MSW	Purox Gas	Oxygen	Slag	Steam	CW	Dolomite	N6 Fuel	Dolime
H ₂							3.86							
N ₂							1.67							
CH ₄			0.13				3.35						4.03	
C ₂ H ₆							1.80							
CO							80.03							
CO ₂			0.35				37.96							
H ₂ O				14.00	1050.00					32.85	1133.07			
O ₂								46.82						
CH ₃ OH														
CH ₃ COOH	99.96	4.76												
0.5CaMg(CO ₃) ₂														
0.5CaMgO ₂														
CMA														
CMA.1/2 H ₂ O														
Totals														
kg/sec/hr	1644.54													
MT/hr	99.96	4.76	16.01	14.00	1050.00	231.33	5952.67	1463.16	69.40	32.85	1133.07	73.09	251.15	38.20
m ³ /hr			358.65	14.00	1050.00		128.66	46.82		32.85	1133.07		4.03	
MSDF/hr			12.67				133339.91	32774.83					5625.72	
							4708.33	1157.30					198.65	

MASS BALANCE - 1 MM aT/yr CMA PLANT - MSM Feedstock

Stream	31	32	33	34	35	36	37	38	39	40	41	42	43
Flowrate (aT/hr)	NG Fuel	CMA Waste water	Total NG Fuel	Total NG	BFM Total BFM	Total CW Mat. rec.	Rec. Gas	Oxygen	Total O2				CO2
H2													
N2													
CH4	5.63			10.45	15.68					3.35			
C2H6										1.80			
CO													
CO2													
H2O													
O2													
CH3OH													
CH3COOH													
0.5C6H6(CO3)2													
0.5C6H6O2													
CMA													
CMA.1/2 H2O													
Totals													
kgole/hr	351.19	792.64		651.37	977.60					268.67	165.01	1628.22	845.17
aT/hr	5.63	126.26		10.45	15.68					5.15	5.28	52.10	37.20
m3/hr	7866.67			14590.66	21898.32					6018.29	3696.14	36472.20	18931.83
MSCF/hr	277.78			515.26	773.33					212.51	130.51	1287.86	668.50

37.20

5.28 52.10

PRELIMINARY CAPITAL COST ESTIMATE
1MM mT/yr CMA Plant - MSW Feed

Nov.18/88

Unit	\$ MM

1. Reformers (Sparg and Autothermic)	18
Off-sites	7
2. Tenneco Cosorb CO Absorption	25
Off-sites	12
3. Lurgi Methanol Synthesis	82
Off-sites	28
4. BP-Monsanto Acetic Acid Synthesis	100
Off-sites	20
5. Selexol CO2 Absorption	20
Off-sites	10
6. Dolomitic Lime Manufacture	30
Off-sites (Included above)	0
7. Gancy CMA Neutralization, Granulation and Drying	33
Off-sites (Included above)	0
8. Union Carbide Purox Plant (incl. Oxygen Plant)	305
Off-sites	65

SUB-TOTAL	755
Contingency (35 %)	264

TOTAL FIXED INVESTMENT	1019
Interest During Construction (15 %)	153
Start-up Costs (2 %)	20
Working Capital (30 d inventory)	30

TOTAL CAPITAL INVESTMENT	1223

PRELIMINARY OPERATING COST ESTIMATE

1 MM mT/yr CMA Plant - MSW Feed

Nov.19/88

FEEDSTOCKS AND UTILITIES

	Units	Cons./hr	\$/unit	\$/yr	\$/mT CMA
Natural Gas	MSCF	773	2.55	\$15,611,508	\$15.61
Dolomite	mT	73.1	7	\$4,052,664	\$4.05
Power	kWh	73000	0.0375	\$21,681,000	\$21.68
Cooling Water	m3	4350	0.0375	\$1,291,950	\$1.29
Boiler Feedwater	m3	150	0.25	\$297,000	\$0.30

SUB-TOTAL

\$42,934,122 \$42.93

CATALYSTS AND CHEMICALS

Reforming				\$105,000	\$0.11
Toluene (CO Unit)	kg	3.92	0.3	\$9,314	\$0.01
Methanol				\$254,000	\$0.25
Acetic Acid (Est.)				\$500,000	\$0.50
CO2 Absorption				\$775,000	\$0.78
Purox Plant (Est.)				\$500,000	\$0.50

SUB-TOTAL

\$1,643,314 \$1.64

LABOUR

	Manpower	\$/man.yr	\$/yr	\$/mT CMA
Operating Labour (OL)				
Shift Foreman	42	\$35,000	\$1,470,000	\$1.47
Shift Operator	148	\$30,000	\$4,440,000	\$4.44
Day Operator	25	\$25,000	\$625,000	\$0.63

SUB-TOTAL (OL)

\$6,535,000 \$6.54

Supervision (OLS) (15 % OL)			\$980,250	\$0.98
Maintenance L. & Supervision (ML+MLS) (80%(OL+OLS))			\$6,012,200	\$6.01
Administration & Support L. (20 % (OL+OLS+ML+MLS))			\$2,705,490	\$2.71
Payroll Benefits (25 % of all labour cost)			\$4,058,235	\$4.06

TOTAL LABOUR COST

\$20,291,175 \$20.29

Maintenance Materials (2.25 % FI)			\$22,927,500	\$22.93
Insurance & Local Taxes (2 % FI)			\$20,380,000	\$20.38
General Overhead (2 % FI)			\$20,380,000	\$20.38
Royalties (Estimated)			\$3,500,000	\$3.50

SUB-TOTAL

\$132,056,111 \$132.06

Contingency (10 %)			\$13,205,611	\$13.21
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TOTAL OPERATING COST

\$145,261,722 \$145.26

Interest (11 % TCI)			\$134,530,000	\$134.53
Depreciation (7.5 % FI)			\$76,425,000	\$76.43

TOTAL PRODUCTION COST

\$356,216,722 \$356.22

Less Credit for Rec. Mat. (Glass, Fe, Al)			(\$15,390,000)	(\$15.39)
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NET PRODUCTION COST

\$340,826,722 \$340.83

CMA Manufacturing Complex - Wood Feedstock

- 1) Preliminary Capital Cost Summary Table
- 2) Preliminary Operating Cost Summary Table

PRELIMINARY OPERATING COST ESTIMATE

1 MM mT/yr CMA Plant - Wood Feed

Nov.28/88

FEEDSTOCKS AND UTILITIES

	Units	Cons./hr	\$/unit	\$/yr	\$/mT CMA
Wood	mT	179.4	60	\$85,250,880	\$85.25
Natural Gas	MSCF	773	2.55	\$15,611,508	\$15.61
Dolomite	mT	73.1	7	\$4,052,664	\$4.05
Power	kWh	73000	0.0375	\$21,681,000	\$21.68
Steam (included in fuel)					
Cooling Water	m3	4350	0.0375	\$1,291,950	\$1.29
Boiler Feedwater	m3	150	0.25	\$297,000	\$0.30

SUB-TOTAL

\$128,185,002 \$128.19

CATALYSTS AND CHEMICALS

Reforming				\$105,000	\$0.11
Toluene (CO Unit)	kg	3.92	0.3	\$9,314	\$0.01
Methanol				\$254,000	\$0.25
Acetic Acid (Est.)				\$500,000	\$0.50
CO2 Absorption				\$775,000	\$0.78
Purox Plant (Est.)				\$500,000	\$0.50

SUB-TOTAL

\$1,643,314 \$1.64

LABOUR

	Manpower	\$/man.yr	\$/yr	\$/mT CMA
Operating Labour (OL)				
Shift Foreman	42	\$35,000	\$1,470,000	\$1.47
Shift Operator	148	\$30,000	\$4,440,000	\$4.44
Day Operator	25	\$25,000	\$625,000	\$0.63

SUB-TOTAL (OL)

\$6,535,000 \$6.54

Supervision (OLS) (15 % OL)			\$980,250	\$0.98
Maintenance L. & Supervision (ML+MLS) (100%(OL+OLS))			\$6,012,200	\$6.01
Administration & Support L. (20 % (OL+OLS+ML+MLS))			\$2,705,490	\$2.71
Payroll Benefits (25 % of all labour cost)			\$4,058,235	\$4.06

TOTAL LABOUR COST

\$20,291,175 \$20.29

Maintenance Materials (2.25 % FI)			\$21,082,500	\$21.08
Insurance & Local Taxes (2 % FI)			\$18,740,000	\$18.74
General Overhead (2 % FI)			\$18,740,000	\$18.74
Royalties (Estimated)			\$3,500,000	\$3.50

SUB-TOTAL

\$212,181,991 \$212.18

Contingency (10 %)			\$21,218,199	\$21.22
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TOTAL OPERATING COST

\$233,400,190 \$233.40

Interest (11 % TCI)			\$123,860,000	\$123.86
Depreciation (7.5 % FI)			\$70,275,000	\$70.28

TOTAL PRODUCTION COST

\$427,535,190 \$427.54

PRELIMINARY CAPITAL COST ESTIMATE
1MM mT/yr CMA Plant - Wood Feed

Nov. 28/88

Unit	\$ MM
1. Reformers (Sparg and Autothermic) Off-sites	18 7
2. Tenneco Cosorb CO Absorption Off-sites	25 12
3. Lurgi Methanol Synthesis Off-sites	82 28
4. BP-Monsanto Acetic Acid Synthesis Off-sites	100 20
5. Selexol CO2 Absorption Off-sites	20 10
6. Dolomitic Lime Manufacture Off-sites (Included above)	30 0
7. Gancy CMA Neutralization, Granulation and Drying Off-sites (Included above)	33 0
8. Union Carbide Purox Plant (incl. Oxygen Plant) Off-sites	244 65
SUB-TOTAL	694
Contingency (35 %)	243
TOTAL FIXED INVESTMENT	937
Interest During Construction (15 %)	141
Start-up Costs (2 %)	19
Working Capital (30 d inventory)	30
TOTAL CAPITAL INVESTMENT	1126

APPENDIX III

ECONOMIC EVALUATION OF A PROCESS FOR CMA
MANUFACTURE BY BACTERIAL FERMENTATION OF SUGARS

SUMMARY

The fermentation of corn derived sugars directly to CMA has not been attempted on the commercial scale. Therefore the SRI process and equipment data were scaled up to our standard size - 1 Mt/a of CMA - plant, and the cost base adjusted to mid-1988, Canadian conditions. The major process modification is the substitution of natural gas fired boilers for the coal fired ones of the SRI design. This reduced the capital cost for the boiler plant and eliminated the need for flue gas desulphurization (FGD). The calculated total capital investment was approximately \$850 MM, including 35% contingency and for \$138/tonne (\$3.50 per bushel) corn the net production cost was about \$530/tonne of CMA.

CMA Manufacturing Complex - Corn Feedstock

- 1) Flow Diagram - SRI Design
- 2) Preliminary Capital Cost Summary Table
- 3) Preliminary Operating Cost Summary Table

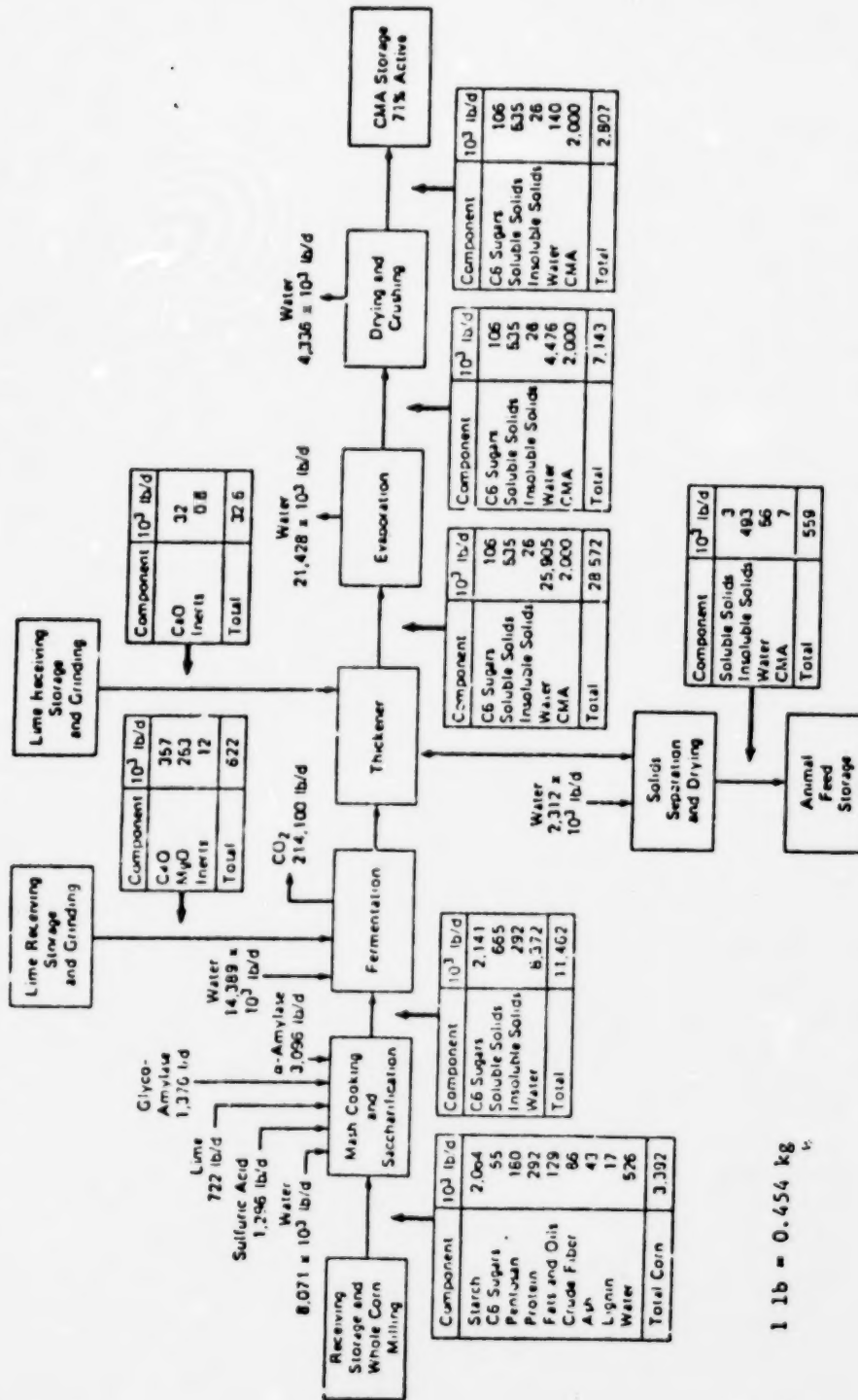


FIGURE 4 BLOCK FLOW DIAGRAM FOR PRODUCTION OF CMA FROM CORN GRAIN

PRELIMINARY CAPITAL COST ESTIMATE
1MM mT/yr CMA Plant - Corn Feed

Nov. 22/88

Unit	\$ MM

1. Dolime receiving and storage	9
2. Corn receiving, storage and milling	14
3. Mash cooking and saccharification	30
4. Fermentation and lime slurring	18
5. Insolubles separation and dewatering	27
6. Feed by-product drying	52
7. CMA solution concentration	25
8. CMA drying, flaking and storage	178
9. Boiler plant	48
10. General service facilities	120

SUB-TOTAL	521
Contingency (35 %)	182

TOTAL FIXED INVESTMENT	703
Interest During Construction (15 %)	106
Start-up Costs (2 %)	14
Working Capital (30 d inventory)	30

TOTAL CAPITAL INVESTMENT	853

PRELIMINARY OPERATING COST ESTIMATE

1 MM mT/yr CMA Plant - Corn Feed

Nov.23/88

FEEDSTOCKS, CHEMICALS AND UTILITIES

	Units	Cons./hr	\$/unit	\$/yr	\$/mT CMA
Corn	Bushel	8469	3.5	\$234,760,680	\$234.76
Natural Gas	MSCF	2178	2.55	\$43,986,888	\$43.99
Dolime	mT	39.5	50	\$15,642,000	\$15.64
Power	kWh	38900	0.0375	\$11,553,300	\$11.55
Water	m3	1400	0.2	\$2,217,600	\$2.22
Enzymes	kg	388	3.85	\$11,830,896	\$11.83
Sulphuric acid	mT	0.82	99	\$642,946	\$0.64
Quicklime	mT	2.07	80	\$1,311,552	\$1.31

SUB-TOTAL

\$321,945,862 \$321.95

LABOUR

	Manpower	\$/man.yr	\$/yr	\$/mT CMA
Operating Labour (OL)				
Shift Foreman	20	\$35,000	\$700,000	\$0.70
Shift Operator	120	\$30,000	\$3,600,000	\$3.60
Day Operator	20	\$25,000	\$500,000	\$0.50

SUB-TOTAL (OL)

\$4,800,000 \$4.80

Supervision (OLS) (15 % OL)	\$720,000	\$0.72
Maintenance L. & Supervision (ML+MLS) (80%(OL+OLS))	\$4,416,000	\$4.42
Administration & Support L. (20 % (OL+OLS+ML+MLS))	\$1,987,200	\$1.99
Payroll Benefits (25 % of all labour cost)	\$2,980,800	\$2.98

TOTAL LABOUR COST

\$14,904,000 \$14.90

Maintenance Materials (2.25 % FI)	\$15,817,500	\$15.82
Insurance & Local Taxes (2 % FI)	\$14,060,000	\$14.06
General Overhead (2 % FI)	\$14,060,000	\$14.06
Royalties (Estimated)	\$2,000,000	\$2.00

SUB-TOTAL

\$382,787,362 \$382.79

Contingency (10 %)	\$38,278,736	\$38.28
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TOTAL OPERATING COST

\$421,066,098 \$421.07

Interest (11 % TCI)	\$93,830,000	\$93.83
Depreciation (7.5 % FI)	\$52,725,000	\$52.73

TOTAL PRODUCTION COST

\$567,621,098 \$567.62

Less By-product Credit (Animal Feed @ Corn Price)	(\$37,930,000)	(\$37.93)
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NET PRODUCTION COST

\$529,691,098 \$529.69